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Development of Registration Criteria for Controlled Release Pesticide Formulations

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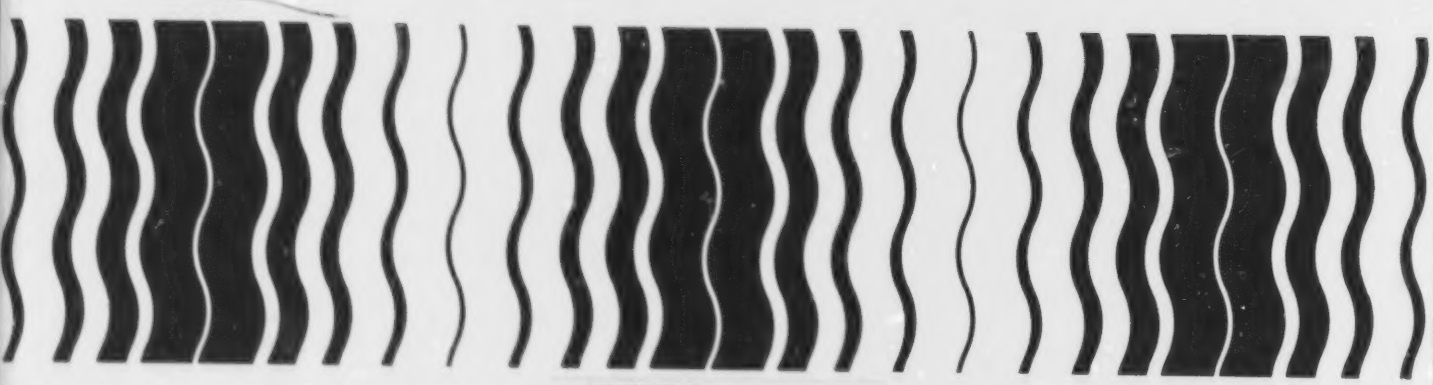

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16. ABSTRACT

This report provides state-of-the-art information on controlled release (CR) pesticide formulations, their efficacy, and materials used in their manufacture. Formulation ingredients and their function are described. Theories of release rate kinetics of various CR systems studied are discussed. 114 pesticides and other agents used in CR applications, 100 materials used in binding matrixes and wall membranes, and 86 additives are listed with their manufacturers, toxicity, and pertinent literature citations. Speculation on degradation products of polymers and additives is offered in the absence of experimental data on environmental effects. Polymers are divided into 15 categories, their properties defined, and degradation rates estimated to provide their environmental persistence. Modes of degradation of these materials are discussed. 20 ASTM test procedures adapted to assessing environmental impact plus other sources of methodology are suggested. 17 procedures in the EPA proposed guidelines (Fed. Reg. 6/25/76) for registering pesticides and other procedures are suggested for study regarding development of appropriate tests for assessing decomposition and aging properties of polymers and additives. Criteria for EPA registration of controlled release products are recommended including efficacy, safety, and toxicological evaluation along with unknown effects of chronic exposure to non-target organisms and systems.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Controlled release pesticides Polymer Binding matrixes Antifoulants Molluscicides Insecticides Herbicides Fungicides Pesticide Additives Rodenticides Nematicides Algicides Predacides Repellents Fertilizers Plant Nutrients	Controlled Release Pesticide Formulations	

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DEVELOPMENT OF REGISTRATION CRITERIA FOR CONTROLLED RELEASE PESTICIDE FORMULATIONS

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SUMMARY

Responsible authorities agree that sufficient food and fiber to support the world's population cannot be produced without pesticides. Yet safety considerations and efforts to improve our environment are imposing additional requirements on the pest control practices that have proven so very effective in the past. Granting that pesticides must be used, they should be used wisely. This report dealing with controlled release pesticide formulations is directed toward this end.

If one considers the present state of the art of pest control methods, it is noted that the nonpersistent nature of many conventional pesticides requires that they be applied in excessive amount in order for them to remain effective for a reasonable period of time. Such applications result in a period of overdosing of the pesticide followed by a period of underdosing. Subsequently, the pesticide has to be applied frequently to maintain satisfactory pest control.

Controlled release pesticide formulations offer the possibility of achieving acceptable or improved pest control by releasing low levels of pesticide (which may already be EPA-registered in conventional formulations) at a fairly uniform rate over a prolonged time interval. In this way, satisfactory protection from pests is attained for longer periods of time with fewer applications and overall smaller quantities of the slow-release pesticides (compared to conventional ones). Thus, the slow-release pesticides are utilized more efficiently and with greater safety (considering that lower levels and smaller quantities of pesticide are needed) to non-target organisms, including man, and the environment.

To illustrate this point, the potent insecticide methyl parathion is lethal to humans at a relatively low level of exposure, so that workers cannot enter sprayed areas for at least one day and then only with elaborate protective garmentation. The same insecticide encapsulated, known as Pencap M^{R}, can be handled with less precautions, and workers can enter sprayed areas 24 hours after treatment without protective clothing. In addition, Pencap M requires fewer applications (compared to conventional formulations of methyl parathion), smaller amounts of insecticide, and is less harmful to wildlife.

The trend toward reduction of use of pesticides has increased interest in the use of controlled release (CR) products like Pencap M. Within the past year, a national and an international symposium were held on controlled release formulations, and two other symposia are scheduled within the next year. Also, a number of controlled release products is being submitted to the Environmental Protection Agency for registration.

This contract has been let to acquire current state-of-the-art information on CR formulations, their efficacy, the materials used in their manufacture, and the environmental impact of the various ingredients. This background information, brought together in one compilation along with more than 500 references, will be useful in generating recommendations for establishing criteria to be used in future registration of CR pesticide formulations.

Controlled release pesticide technology can be defined as the release of a pest control agent from a polymeric carrier, binder, absorbent, or encapsulant at a slow continuous effective rate into the environment. Output is prolonged (from weeks to perhaps years) in contrast to the short-time effective interval common to many conventional pesticide formulations. Release rate kinetics of various CR systems have been studied and found to vary with the particular system. Theories developed over the past decade are discussed in this report and will provide guidance in predicting release rates in many instances.

Registered CR formulations in use today are comparatively few. Because information concerning the environmental behavior of CR formulations is generally inadequate, careful testing of these formulations will be necessary to answer a number of questions before registration will be granted. For example, once a long-acting pesticide formulation is applied to a field crop, it cannot be withdrawn to stop its action if a deleterious effect should be discovered. A short-acting material will simply dissipate itself quickly. On the positive side, some believe CR formulations may give the long-lasting effects characteristic of the persistent pesticides (some of which have been withdrawn from use) without their inherent disadvantage of bioaccumulation in mammals (including man).

Aside from the economic advantages of reduced amounts of pesticide required for pest control and the fewer number of treatments, some (but not all) CR formulations have demonstrated in experiments another unexpected advantage. Extremely low concentrations of pesticide continuously applied over periods of weeks or months have destroyed target pests (generally organisms living in water) without harm to coexisting biota. This so-called "chronicity" effect indicated that destruction of pests can sometimes be achieved more efficiently and with smaller amounts of pesticide at chronic levels than with the acutely toxic doses common to conventional (and certain CR) treatments. There are few reports on the effects of low-level pesticide treatment; however, where applicable, this low-level treatment may be the method of choice for pest control, one less damaging to wildlife and the environment. Amount of pesticide in a CR treatment may sometimes be higher than that used in a conventional treatment. However, most of the pesticide is locked into the CR formulation initially, and the pesticide is gradually released. Accordingly, "available" pesticide residues in the environment are expected to be low. Use of nonpersistent pesticides should further preclude accumulation of pesticides in wildlife and the environment.

CR formulations share a common problem with conventional pesticides--the toxicology of most of the formulation ingredients other than the active ingredient has not been examined in great depth, nor has their environmental impact been evaluated. With CR pesticides, the polymeric materials and many of the additives are expected to be persistent, and though most of these are not expected to be hazardous to man and the environment, knowledge of the amount and nature of the residues, metabolites, and general fate of these materials remains largely unknown.

State of the Art

This report presents specific information on the state of the art of a wide variety of CR pesticides. As in many new fields of endeavor, most reports on CR products are experimental in nature. Nevertheless, there has been considerable progress in improving CR products, and much activity in this field has been noted. In addition, an understanding of the mechanisms of pesticide release and the function of individual ingredients is helping in the design of new products that are more efficacious and safe. Whenever possible, formulation ingredients and their function have been described.

Controlled release formulations have been particularly important with some of the newer pesticidal agents, such as the juvenile hormone mimics and the sex attractants (pheromones). These materials are generally very expensive compared to conventional pesticides; however, they are very potent, and in certain instances, their CR formulations can suppress or help suppress pests economically enough to compete with conventional pesticides or substantially improve their action. Major advantages here are the highly specific action of these materials on the target pest and the lack of effect on non-target biota or persistence in the environment.

Controlled release technology is widely used for dispensing insect sex pheromones. For the traps used in monitoring the whereabouts of insects, several types of dispensers have been devised to adjust pheromone release rates to optimum levels for prolonged periods to achieve maximum captures. Encapsulation of sex pheromone solutions and a number of other slow-release techniques have been used to permeate the air with pheromone in order to disrupt communication between the sexes and thereby prevent mating. Thus, many insect species follow air-borne pheromone trails to find the opposite sex for mating. This mechanism can be upset by broadcasting the CR formulation to release and maintain a sufficient level of pheromone in the atmosphere for the entire mating season (a week to many months). Pheromones have now been identified for many important economic pests. What is lacking in most instances are effective CR formulations and associated technology to utilize these chemicals in direct pest control.

Controlled release formulations of conventional prestICIDES have likewise been developed. Insecticide-polymer mixes have been successful against mosquito larvae. Encapsulated insecticide (e.g. Pencap M) has proven to be successful in terms of efficacy, safety, and environmental acceptability. The well-known "No-Pest Strip" is a CR device that dispenses dichlorvos. New on the market is "Roach Tape" (product of Johnson Wax), a 3-layer laminate that continuously "bleeds" insecticide from its central layer to the exposed surface. Control of roaches is effected by their contact with the insecticidal surface of judiciously placed 1" x 4" strips in kitchens and bathrooms. The U. S. Army Corps of Engineers has sponsored development of CR herbicides that will keep waterways from being choked by aquatic weeds.

A total of 144 pesticides and similar agents used in CR applications along with their manufacturers (when known) and pertinent references to their use have been assembled (Table 3). The listed materials appear to be largely pesticides in conventional use, or attractants, which are used in small amount and generally considered harmless. Materials (about 100) used in the binding matrix and wall membrane (Table 4) and 86 additives (Table 5) of CR formulations have also been listed with their manufacturers (when known), toxicity (often estimated), and pertinent literature citations. Some of the additives are no longer acceptable to EPA currently. However, substitutes can undoubtedly be found.

Section VI describes 20 CR products that have been developed. Compositions or partial compositions, uses, and other pertinent matter related to these products are given. The CR materials include insecticides for field and home use, herbicides, insect growth regulators, insect attractants, molluscicides, algicides, and bactericides. Four controlled release systems and products or potential products utilizing these systems are also described.

Environmental impact of Polymers and Additives

Though data found in the literature dealing with the protection of polymers from the environment are numerous, virtually nothing was found on the effect of polymers on the environment. In the absence of hard data, speculation on products that might be expected in the deterioration of the polymers and additives in CR pesticide formulations has been offered. However, with very little of the formulation normally being dispensed (fraction of a pound to a few pounds/acre/yr), with degradation of these mostly organic materials being slow, and with virtually no demonstrated toxicity associated with these materials, it is difficult to visualize the occurrence of any deleterious effect of CR formulations on non-target biota or the environment. Polymers are divided in this report into 15 categories, the properties of each are defined, and their rates of degradation estimated to provide some idea of persistence in the environment. Mode of degradation of these materials is also discussed.

Additives modify the behavior of polymeric or other matrices used to dispense the pesticide. These materials, generally regarded as innocuous because they are not active agents per se, vary greatly in chemical composition, function, and in degradative properties. The additives help control release rates, aid in frabrication, protect the accompanying polymer against insolation, oxygen, moisture, etc., and they aid in dispensing the formulation (e.g. thickeners and stickers). A listing of 83 of the additives and, again in the absence of hard data, an opinion of their environmental impact are given in Table 10.

Test Procedures and Criteria

There appear to be no uniform tests or criteria established to measure the environmental impact of CR pesticide formulations. In such assessments, the quantity of formulation used as well as its composition must be taken into account. With knowledge of the formulation ingredients, their functions and properties, it should be possible to modify formulations to enhance their environmental acceptability, e.g. by speeding the decay of persistent ingredients.

With methods for assessing environmental impact not available, 20 ASTM test procedures that may be adaptable to this purpose and a number of other sources of methodology have been suggested, e.g. there are tests for accelerated aging of rubbers or plastics, changes in properties resulting from liquid immersion, artificial weathering, and resistance to heat, ozone, bacteria or fungi. Part of the difficulty here is the undefined and diverse nature of the environmental forces themselves that may act upon the CR materials. Thus, the end use will have to be considered in the decision on the tests to be applied to a CR product. In final tests, environmental impact may have to be based upon tests in individual locales, although it may be possible to derive considerable information from laboratory-type tests that include evaluation of physical, chemical, and biological (toxicology included) properties of active and "inactive" ingredients, both separate and combined. Seventeen procedures in the EPA proposed guidelines (Fed. Register June 25, 1976) for registering pesticides and a number of other procedures have been selected as worthy of study in regard to developing appropriate tests for assessing decomposition and aging properties of polymers, additives, and their combinations. Among these are degradation in water, leaching, photodegradation, stability, soil metabolism and persistence, and effect of microorganisms.

Conclusions and Critique

Since the complete elimination of conventional synthetic pesticides is unrealistic, methods advanced to minimize pesticide pollution should be explored continuously. Biological control methods as well as cultural practices are often desirable, but their applicablity is as yet largely limited in today's agricultural practice.

Improved pesticide formulations and dispensing systems, more specifically, those employing CR technology, do offer a viable means of achieving satisfactory or improved pest control in many instances with seemingly no damage to the environment. This is a more sophisticated approach than the current conventional heavy-dosing with pesticides because the low-level long-term release of CR pesticides is designed to eliminate pests and yet be harmless to non-target biota or systems. CR formulations may also reduce the development by pests of resistance to pesticides because heavy dosing is not used. Laboratory and field trials have shown CR formulations are effective in many instances, and some CR products are now on the market. Of course, if rapid action is required, as occurs with a sudden pest buildup, conventional treatment is generally indicated. However, where they can be operative, CR formulations have some significant advantages over conventional formulations; e.g., decreased hazard in handling and use, fewer pesticide applications and overall less chemical required for control.

As far as registration of CR products by EPA is concerned, to some extent each product will have to be considered individually, e.g., in regard to its efficacy and safety. During this study, it has been found that many of the additives in CR formulations are also used in approved conventional formulations. Though this does not ensure their safety, it does relegate an investigation of these materials to a lower priority. EPA is presently undertaking a detailed study of "inert" ingredients to investigate the present adequacy of registration requirements. Many of the other inert ingredients are polymers which are generally well known to be inert toxicologically and probably environmentally. A few plasticizers and additives may be more suspect from a toxicological viewpoint than an environmental basis; yet, because many of the plasticizers and some of the additives are widely used, a high priority cannot be assigned to the investigation of the materials "generally regarded as safe" simply because they appear in CR formulations. More pertinent to the establishment of criteria for registration are the unknown effects of long-term continuous exposure to low levels of pesticide on non-target organisms and systems. Toxicological evaluations that address this question for both target and non-target species would appear to be desirable, expecially to verify and take advantage of the so-called "chronicity" effect.

Tests (usually of the laboratory variety) that can be modified for use in judging environmental impact have been suggested. They can be studied, and modifications can be appropriately tested to develop desired registration criteria. At this time, no known hazard has been noted in the use of CR pesticides. This might be due to lack of knowledge or data, or simply to inadequate judgment. However, the amount of CR materials (other than the pesticides) destined to be dispensed seems rather small, and therefore the likelihood of any significant deleterious effect on non-target biota or the environment seems remote at this time (1976). Indeed, it is expected that compared to conventional technology, CR formulations will reduce or eliminate many environmental problems, even if the volume of CR formulations approaches that of conventional pesticides.

Because the amount of pesticide used is less in CR formulations than in conventional ones, pesticide manufacturers are not likely to be enthusiastic about promoting the use of CR technology unless they also manufacture the CR formulations (e.g. Pennwalt); however, formulators may develop CR products, and undoubtedly some will be successful.

It would appear to be in the interest of the Environmental Protection Agency to encourage the use and development of controlled release formulations with the proviso that these materials shall be monitored in the field for unforeseen toxicological and ecological effects (which can sometimes occur despite advance testing), especially during initial scale-up in various locales. Information on development and use of CR products should be collected and maintained in a repository, and perhaps summarized and published periodically, in order to aid in the development of CR technology, to detect any possible hazard at an early stage, and to otherwise assure the safe and efficient usage of controlled release pesticides. From present indications, the CR approach offers excellent opportunities for generating products highly beneficial to man and the environment.

I. INTRODUCTION

A. SCOPE OF WORK

This report is submitted under Environmental Protection Agency Contract number 68-01-1922, entitled, Development of Registration Criteria for Controlled Release Formulations. The major task consisted of a thorough literature search on Controlled Release Pesticide formulations focusing on their efficacy, safety and environmental impact. This literature investigation is keyed to the accumulation of data regarding the release rates of active materials from a polymeric carrier and the nature of residues and metabolites arising from environmental degradation of the active agent and other so-called "inert" elements of the formulation. A comparison of the environmental chemodynamics of agents applied conventionally and through controlled release methodology was undertaken. Knowledge concerning persistency in soil and water, microbial degradation, leaching effects, chemical reactions, bioaccumulation, plant uptake, phytotoxicity, and effects on non-target biota has been included where available. The problem of long term continuous exposure of non-pest life to low toxicant concentrations was examined. An important aim of this literature search was to elucidate the environmental impact in terms of persistence, residues, and chemical interactions of the carrier polymer and major formulation additives. The search encompassed data describing the relationship between biological and physical/chemical properties of controlled release formulations and the analytical methodology involved in detecting such relationships.

Task I of the subject contract required a thorough literature search. The second task called for the establishment of a file of the literature reviewed. Thus, referenced items in this report are submitted separately to the Environmental Protection Agency--save standard texts and documents of excessive length. Private interviews were conducted with key E.P.A. personnel and knowledgeable individuals in industry and various institutions. Information generated by such contact is included herein and appropriately referenced in meeting the requirements of task 3.

The final outlined task was to compile all data generated through the aforementioned searches into the detailed report presented here. Environmental and toxicological behavior of controlled release formulations, as it relates to efficacy, safety and impact is presented along with comments and recommendations as apropos for establishing registration criteria for products arising from this new technology.

Although not specific to the general undertaking, several areas of controlled release technology; namely, fertilizers and marine antifoulants, are described because the data generated and principles involved in these endeavors have application to controlled release pesticide formulations.

This report does not attempt to review the voluminous literature concerning the toxicity, chemistry, and environmental impact of toxicants used in conventional formulations--but rather efforts are concentrated only on the much narrower literature regarding controlled release aspects.

B. CONTROLLED RELEASE PESTICIDE TECHNOCLOGY DEFINED

Controlled release pesticide technology can be defined as the release of a pest control agent from a polymeric carrier, binder or encapsulant at a slow continuous effective rate into the environment. The agent may be a toxicant, repellent, or substance modifying pest life behavior in a manner amenable to control.

Controlled release materials differ significantly from conventional pest control formulations in the following manner: Release is usually a long term process occurring over months or years with the active ingredient (a.i.) concentration in the environment very small at a given time reference. However, a.i. output is continuous so that the distinguishing feature of controlled release--low concentration over an extended period-- can be contrasted to the relatively massive a.i. output over a very short time interval as common to conventional pesticide usage.

There are several distinctive types of controlled release:

1. Polymeric Matrix

The control agent is dissolved or dispersed within a solid or liquid polymeric material. Upon exposure to an exterior environment, the active ingredient slowly leaves the matrix, passes through an interface, and enters the surrounding environment.

Polymeric materials take two forms:

a) Plastics (solids) where the agent is contained by mechanical means, i.e. dispersed.

b) Elastomers (liquids) where the agent is held through solution processes or mechanically bound.

Release from a polymeric matrix can be achieved through several means:

a) Diffusion-dissolution wherein molecules of the dissolved agent through solution pressure slowly migrate toward a depleting surface in accordance with the laws of solution equilibrium. Depletion at the interface is due to dissolution.

b) Carrier migration whereby nonsoluble molecules of the active ingredient are moved toward the surface via migration of an encompassing third phase material. The active ingredient may be soluble or insoluble in the carrier. Also the dispersed third phase element may not "move" per se, but serves as a transmission path for the nonsoluble agent.

c) The active ingredient may be mechanically contained in such a fashion or have solubility properties that mitigate against motion, so that the a.i. cannot normally leave the matrix save through degradation, solution or exfoliation of the matrix.

d) Leaching of the agent through an internal pore structure upon contact with water or vapor phase loss to soil or air.

2. Encapsulation

The control agent is incorporated in a solvent or carrier material and overcoated with a polymeric film. Agent release is effected by several mechanisms.

a) Permeation of the film barrier

b) Physical rupture of the film barrier

c) Chemical degradation of the film barrier

3. Reaction Products

Pendent pesticidal moieties bonded to polymeric molecules are cleaved through chemical reaction with the environment and thus pass into that environment.

4. Baits

Destruction of undesirable animal life through the use of baits is a well-known control technique. Bait formulations are essentially controlled release wherein a toxic additive is tightly bound and a nontoxic element slowly released into the environment. The target organism detects the presence of the bait and, as for rodenticides, the organism ingests a lethal quantity. In more sophisticated systems, a contact poison may be utilized and actual feeding is unnecessary. In some instances, the bait releases an attractant and the target insect, slug, etc. in seeking the source is mechanically trapped.

C. THEORY

A considerable body of theory has been developed over the last ten years both to explain observed effects and to serve as guidance for future product development and environmental considerations. Release rate kinetics vary from system to system. Encapsulated pesticides or attractants are generally zero order, dissolved systems almost always show an initial release proportional to $t^{-1/2}$ and then a sustained release in accordance with e^{-t}, whereas dispersed systems follow $t^{-1/2}$ (t=time). Baker et al. have provided a mathematical summary illustrating these distinctions.[1]

Early work by Desai et al. regarding controlled release of medicinals from various homopolymers showed that release rate was affected by the solubility parameters of the agent, additives used, porosity and tortuosity of the matrix and the polymer type.[2] This work was extended to show that the boundary diffusion layer was an important element in release.[3] Harris, in his development of controlled release herbicides, has shown the essential correctness of the aforementioned studies in this respect.[4] The effect of pellet or granule geometry on the rate of agent release has been described by Collins for model systems.[5] Importantly the theoretical work of Collins and Doglia has shown that the long term behavior of a non-persistent agent release via controlled release methods is similar to that of a more persistent agent with a smaller first order rate constant.[6] Controlled release, in a sense, adjusts the pesticide release rate to a uniform level over a selected time interval thus allowing more efficient use.[7]

In systems where the agent is soluble in the polymeric matrix either diffusion or dissolution may be rate controlling. In the former case various matrix parameters influence the diffusion coefficient and thus the release rate. Kanakkanatt has shown experimentally the dependence of molluscicide diffusion in various elastomers upon crosslink density, glass transition temperature and other matrix properties.[8,9] It is observed that with appropriate knowledge of the matrix one can calculate release rates. If both the molecular weight of the polymer used and the pesticide loading affect release rates in systems where the agent is soluble in the matrix is known, then release rates can be predetermined.[10,11] There is even indication that controlled release materials of this nature can be designed by computer.[11]

Agent loss rates in soils are not as well understood. Chandrasekaran et al. have mathematically determined the kinetics of agent transport from diffusing systems.[12] The special case where the binding matrix degrades through interaction with soil moisture has also been theoretically investigated.[13]

Whereas various investigators have described model systems and logically established a theoretical basis for CR (controlled release) systems, there is an almost complete lack of confirming field studies. Exceptions to this generalization will be considered later as the various CR products are described.

D. PROBLEM AREAS

The use and potential use of controlled release agents will predictably lead to a number of environmental problems. For example, once a long-acting pesticide formulation is applied to a field crop, it cannot be withdrawn if a deleterious effect should be found. It is assumed that such materials will display appropriate biological efficacy (else they will never achieve commercialization) and, in general, CR formulations are less hazardous to humans in handling than if the same agent were used in the conventional sense.

1. Chronicity Phenomenon

The economic advantage of controlled release lies in the extension of between-treatment intervals, a better spacing of such intervals and continuous pest protection. However, in many instances it will not be practical to maintain adequate toxicant concentrations at the conventional usage load for long periods of time. Both the economic burden and the environment impact could be undesirably great. For instance, a given agent may be added to water to control pest insects, aquatic weeds, or other pests, at several parts per million. Long term maintenance of 2-ppm toxicant concentrations in static water would require literally tens or hundreds of pounds of the CR material per acre foot. Economic considerations would probably dictate no more than a few pounds per acre. Treatment of flowing water and long term maintenance of several ppm would possibly necessitate thousands of pounds of the CR material. Therefore, it is believed that a maximum practical continuous toxicant concentration would be 0.1 ppm or less in static waters, possibly 0.05 ppm in soil, and no more than 0.01 ppm in flowing waters--based upon our present knowledge of controlled release formulations and assuming that months of release are required. There are exceptions, of course. Only several weeks release of an agriculatural herbicide may be optimal, and certainly four or more years of release is desirable for marine antifouling formulations.

Thus, for CR systems to be practical, the target organism may well have to be controlled at dosage levels considerably lower than that necessary via the conventional application methodology.

A belief developed and practiced, especially in field applications, over the years has been that weed, snail and insect pests will succumb to toxicant exposure in accordance with a Ct (concentration X time) relationship, i.e., if 1 ppm exposure kills in 24 hours, a 2 ppm exposure will provide the same results in 12 hours while 0.5 ppm requires 48 hours, and so on. Most laboratory bioassays do not look beyond about 96 hours exposure and, as a rule the Ct relation holds over at least a practical toxicant usage range. However, field studies have long indicated that the residual control agent will provide suppression of target life for weeks after most of the available toxicant has been lost.

It has been discovered during the development and evaluation of controlled release formulations that ultralow toxicant concentrations will destroy pest life if exposure is continuous over a period of weeks or months. This was initially observed during the evaluation of controlled release aquatic herbicides.[14] As an example, Table 1 illustrates the LT_{99} (time to 99% destruction of the target organism) for various concentrations of diquat herbicide bioassayed with Eurasian watermilfoil, *Myriophyllum spicatum*.

TABLE 1
Effect of Various Concentrations of Diquat*
Aquatic Herbicide on Eurasian Watermilfoil[15]

Diquat Conc. (Constant)	LT_{99} for Eurasian watermilfoil
1.000 ppm	11 days
0.100 ppm	19 days
0.010 ppm	16 days
0.001 ppm	32 days

*See Chapter 3 for chemical terminology. Trade or trivial names are used herein for brevity.

Similar results were observed in laboratory evaluation of Silvex, 2,4-D acid, various esters of 2,4-D, Fenac, Endothall, and Fenuron in tests against *Vallisneria americana*, *Cabomba caroliniana*, *Elodea canadensis*, *Najas guadalupensis*, *Pistia stratiotes*, *Eichornia crassipes* and other water plants.[16, 17, 18] The Ct relationship obviously did not hold at low concentrations for long term exposures. Similar results have been seen in the bioassay of various molluscicides against snails,[19,20] controlled release insecticides against mosquito larvae,[21,22] and in other instances to be discussed.

It has thus been postulated that long term exposures to ultralow toxicant concentrations lead to a terminal *chronic* intoxication as opposed to the *acute* intoxication syndrome observed in the use of pesticides in the conventional manner as regards specific pesticide/pest interactions.[17,19,23] The terms "chronicity" and "chronicity phenomenon" were coined in contradistinction to the Ct relationship. However, the existence of a chronic effect was certainly implied by Shaw et.al. as early as 1960.[24] It is by no means implied that this phenonmenon is universal in application.

The chronicity mechanism is unknown. Cardarelli has postulated, based upon the theory by Dinman that stochastic determinants impose a limit to dose-response relationships,[25] that plant protective mechanisms are not triggered by ultralow toxicant exposures and thus normal physiological barriers to herbicide uptake are not present.[23]

Whereas the chronicity phenomenon can be demonstrated to be real under both laboratory and field conditions in certain instances, it may represent a mixed blessing. Obviously a major advantage arises from the absolute need for less control agent and thus less overall quantity of a toxic element being added to the external environment. However, the impact of the *continuous* presence of even a minute amount of a given agent is largely unknown. Investigations of the past have concentrated upon the results of relatively large dosing for very short time spans. Long term data is sadly lacking--especially for non-persistent (and usually environmentally preferred) pesticides since in the conventional sense they rapidly degrade. Although a number of potential problems can be hypothesized--the two basic unknowns remain--(1) *What is the effect of continuous low level toxicant exposure on non-target biota, including man; and (2) will such exposure result in a growing tolerance to that agent among target populations?*

2. Formulation Additives

Controlled release materials are generally formulated from three components--agent, polymer and various additives.[26] In a given formulation such additives usually comprise only a few percent by weight. The trend seems to be that investigators, industry, and registration authorities either ignore their potential impact or assume inertness. So far as can be determined the components of a given material considered in terms of environmental contamination have been limited to the control agent. The polymeric binders usually have been exempted from tolerances, as are agent carriers--such as solvents.

Several categories of additives are used in controlled release products and their use is essential to impart desirable physical properties to the binding matrix, or in a few instances, to regulate agent loss rate. These include plasticizers, vulcanizing (crosslinking) agents, vulcanization accelerators, antioxidants, antiozonants, biocides to prevent microbial degradation, reinforcing agents, colorants, dispersants, processing aids, bulk fillers, wetting agents and others. Such materials, though present in relatively small quantities are often biocidal, for instance various thiurams, mercaptobenzenes, alkylphthalates, etc. One common additive, an antioxidant, phenyl-B-napthylamine, has recently been withdrawn from the market as a suspected carcinogen. As will be discussed, most additives have never been thoroughly evaluated relative to human safety (following long term exposure) let alone their environmental impact.

3. Persistency and Residues

Attention has inevitably been focused upon the environmental fate of the active agent. It is noted that in the case of CR pesticides, the polymeric materials and many of the addivites are relatively highly persistent. Breakdown products arising from chemical, biological or photolytic reactions are generally unknown as to structure or toxicity. Some polymeric materials may be environmentally active although they appear to be inert. Poly(vinyl chloride) appears very stable in soil and water, and has a long life as attested by numerous commerical products--such as drainage and sewage conduits. Does it release vinyl chloride during the very slow chemical deterioration? Many additives such as sulfur, carbon, zinc oxide etc. are probably quite innocuous. What happens, however, to dioctylphthalate in soil, water or air?

The intent of this report is not to play the devil's advocate. The authors feel that most polymers and most additives have very little environmental impact. However, it is recognized that the degree and nature of that impact is just not known--and therefore the problem of our inadequate knowledge must be addressed.

* * *

In order to fully discuss the three enumerated problems it is essential that the state of the art regarding controlled release pesticides be known. The next chapter is devoted to summarizing current investigations, data demonstrating efficacy and safety, and what little is known regarding environmental impact of formulation components other than the toxic agent.

II. STATE OF THE ART

A. ANTIFOULANTS

Antifouling coatings comprise the oldest known form of controlled released pesticides. Their developmental sequence can be traced back to 700 B.C. and possibly earlier. Modern conventional antifouling paints are composed of a toxicant, cuprous oxide being favored, which is mechanically held within a polymeric vehicle such as a polyacrylic, polyamide, polyester, chlorinated polyisoprene, polyurethane, etc. Often the vehicle is modified with wood rosin or other materials. The Cu_2O loss mechanism is by leaching or exfoliation, the former predominating. Copper paint characteristics are (1) relatively short life, (2) massive use of the agent--about 85% to 96% by weight of the dried film, (3) necessity of protective primers--red lead being popular-- to prevent establishment of a copper-iron galvanic couple leading to accelerated corrosion of the underlaying metal substrate, and (4) generally poor adherence, tensile strength, abrasion resistance, and so on.

In 1964 one of the authors (NFC) discovered that certain organotin compounds having an antifouling character could be incorporated in various elastomeric materials, such as the chloroprenes (Neoprene WRT et.al.), and a controlled release antifouling surface created.[27] A relatively low agent loading, 2% to 8% bis(tri-n-butyltin) oxide, tributyltin fluoride or tributyltin acetate, incorporated in chloroprenes, natural rubber, polyisobutylene, polyurethane, styrene-butadiene polymers or acrylonitrile rubber, provided very slow toxicant release over a prolonged time period. Organotins were found to be soluble in many elastomers, and a biologically efficacious loss rate was established through proper compounding. The mechanism of loss, diffusion-dissolution, has been amply demonstrated.[27,28] Unlike conventional antifouling paints the toxicant loss rate and thus biological efficacy was found to be scientifically predictable based upon the equations governing solution equilibrium.

The initial use of the material, now commercialized as NOFOUL^tm^, was in sonar domes and later as sheet coating adhered to ship hulls, buoys and other submerged structures.[29] NOFOUL^tm^ rubber has shown long term biological efficacy, approaching ten years of continuous toxicant release with the first commercial buoy coverings.[31-32] Although not yet put into practice, it has been shown that a composite system utilizing a highly absorbent reservoir elastomer containing a relatively high organotin loading covered with a thin polymeric release-regulating membrane could provide extremely long term release--perhaps measured in decades.[33]

Woodford and others in Australia have likewise incorporated bis (tri-n-butyltin) oxide, tributyltin fluoride and tributyltin acetate in rubber and achieved promising long term biological protection.[34,35] It has been demonstrated that the tributyltin fluoride material is superior to the others and thus it is expected that the U. S. market will soon recognize that fact.

The development of longer lasting paint type coating continues in that the high materials and application cost for NOFOUL^{tm} sheet material renders it economically unacceptable for most uses. Organotin paints, initially showing very poor lifetimes, have now been developed to the point where they are displacing cuprous oxide materials. Tributyltin fluoride is probably the superior toxicant for antifouling paint compositions, although bis(tri-n-butyltin) oxide paints are in wide usage, and triphenyltin chloride, triphenyltin hydroxide and triphenyltin fluoride are under investigation.[36] Although studies of other novel toxicants, such as 10',10-oxybisphenoxarsine, have been performed or are underway, it is believed that the organotin, and conceivably organolead, materials will come to the forefront for antifouling use.[26] One non-metallic material, tetrachloroisophthalonitrile, incorporated in controlled release paint or sheet type coating, is now commercially available. Due to the safety and reduced environmental contamination, this may be a leading future contender in the antifouling area.

Organolead materials, especially triphenyllead acetate, have demonstrated good antifouling potential and, when properly formulated in polyvinyl chloride/polyvinyl acetate copolymers as a paint coating, have shown five or more years efficacy.[37] It has also been demonstrated that the organoleads can be polymerized into toxic macromolecules and that organolead synergizes cuprous oxide activity in paints.[38]

It has long been known that the organotin agents released from antifouling rubber are not identical to those incorporated during processing. In NOFOUL^{tm}, bis(tri-n-butyltin)oxide is the added agent while three or more organotins are lost upon immersion. Chromatographic evidence indicates that tributyltin dilaurate, dibutyltin oxide, and tributyltin sulfide are released along with other unidentified tin-bearing materials. Organotins are reactive with fatty acids, sulfur compounds and amines. During processing the batch mix is subjected to elevated temperatures and high pressures thus enhancing the possibility of reaction with compounding ingredients. It has also been demonstrated that organotins will crosslink chloroprene molecules under processing conditions.[39] Recently Carr and Kronstein have shown that triphenyl lead acetate, in a vinyl copolymer or vinyl copolymer-wood rosin vehicle, is lost as a reaction product upon immersion[40], i.e., the antifoulant is not the agent added but a chemical combination of that agent with the film forming matrix element.

Organoleads have also been incorporated in elastomeric based paints utilizing polyurethane, polybutadiene and polyacrylonitrile polymers.[41]

Considerable work is in progress wherein the organotin or other toxicant is grafted to a polymeric backbone. Upon immersion, such materials slowly lose their pendent substituent to the polymer/water interface thus repelling fouling. Akagane and Matsuo showed that pentachlorophenol and triethyltin hydroxide could be reacted with a copolymer of styrene-maleic anhydride, and upon immersion the toxic moiety was gradually lost through hydrolysis.[42] They mathematically demonstrated an absolute distinction between conventional loss; $Ln\frac{L}{L_o} = -Dt$ where L_o = initial loss rate and D the diffusion constant, and loss from polymeric toxicants where $L = K_o(e-kt - e-Dt)$, K_o being an experimental constant and k the hydrolysis constant. Dyckman *et.al.* developed organotin addition products of acrylic, vinyl and cellulose polymers.[43] It has been shown that such materials, upon exposure to the marine environment are hydrolyzed, thereby releasing toxic organotin materials at a slow rate.[44,45] Dunn and Oldfield have also developed a covulcanizate using an organotin monomer (tributyltin acrylate) + an elastomer + a peroxide that likewise exhibits good antifouling properties.[46]

In summation, controlled release antifouling coatings and coverings have been shown to be biologically efficacious, long lasting (up to 9 or more years) and economically attractive for some uses. The diffusion-dissolution technique and the concept of slowly hydrolyzing pendent substituents are shown to be practical. From the environmental impact consideration and the registration criteria, two problems arise. These are the effect of low concentration but continuous long term release, and (probably more important) the fact that the toxicant added and so labelled may not be the toxicant released. The progress in antifouling technology is admittedly of minor importance compared to progress in the insecticide and herbicide areas; however, the methodology, theory, concepts, and environmental problems arising in this older area will carry over into other areas of immediate concern.

B. MOLLUSCICIDES

Molluscicides are materials toxic to snails and slugs. Both consume garden crops and thus are agricultural pests. Much more importantly, over 80 species of snails transmit parasites that infect man. The major parasitic disease in the world today is Schistosomiasis, with perhaps 300 million sufferers. Other than in Puerto Rico, the United States does not have active transmission of *Schistosoma mansoni*, *Schistosoma hematobium* or *Schistosoma japonicum*. Of course there are many thousands of infected Puerto Ricans, Yemeni, and others living in the U. S.

In the Great Lakes area and along the coast various forms of Schistosome dermatitis are found and represent a nuisance. The common names are "swimmers itch", "clam diggers itch" and the like. Such infections arise when man intervenes in a fish-snail or bird-snail cycle. Although the cercaria of the parasite cannot survive in the human body, the attempted penetration of the dermis leads to an allergic reaction of varying severity. A few deaths per year are recorded--usually in Michigan, Wisconsin and Minnesota.

Conventional molluscicides include copper sulfate, copper pentachlorophenate, sodium pentachlorophenate, trifenmorph (N-tritylmorpholine), and niclosamide. Copper sulfate and niclosamide are used to control swimmers itch in recreational areas.[47,48] Use in Michigan alone (1969) comprised 57,050 lbs. of copper sulfate and 21,500 lbs. of niclosamide.[49]

It has been recognized for some time that various organotins are molluscicidal.[48-50] Tributyltin acetate and tributyltin chloride provide longer residual life compared to niclosamide and copper sulfate.[53] Nine months activity from one treatment has been reported.[54] Downstream movement of organotins from one application site is about equal to that of niclosamide.[55] In the only known field test under dynamic water conditions, bis(tri-n-butyltin) oxide effectively destroyed snails.[56] In general there has been little acceptance in the use of organotin materials as molluscicides in the conventional sense, although their use has been advocated.[57]

Various nitrosalicylanilides are molluscicidal, and one specific material, the ethanolamine salt of niclosamide (5,2'-dichloro-4-nitrosalicylanilide), has seen widespread usage around the world as well as in the United States.[48,55,58,59]

Recently organolead materials have been observed to be molluscicidal.[37,60]

1. Controlled Release Molluscicides

In 1964 it was discovered that organotin containing elastomers were toxic to snail transmitters of Schistosomiasis and Schistosome dermatitis, and a developmental program was established keyed to the creation of a long term environmentally safe controlled release molluscicide.[61,62] Niclosamide was likewise incorporated in various elastomeric materials and formulated to release for many months following immersion.[61,63] Methods were developed for increasing the amount of toxicant in the matrix through adding various absorbing materials.[65] Other molluscicides added to elastomers and a diffusion-dissolution method of release established include tetrachloroisophthalonitrile and 3,3,4,4-tetrachlorotetrahydrothiophene-1,1-dioxide.

A commerically attractive organotin molluscicide, containing 6% bis(tri-n-butyltin)oxide, was developed for the M & T Chemical Co. by the Creative Biology Laboratory.[66] This material has been commercialized as BioMet SRM and sold overseas for snail control.[68] Likewise, a controlled release copper sulfate material has been developed for the International Copper Research Association, and is available in pilot plant lots for commercial use under the trade name INCRACIDE^{tm} E-51.[68-70] This product functions through a leaching type release system and has a limited release life of 6 to 10 months.

Controlled release niclosamide materials have been developed and show some promise.[66,71]

Organotin releasing elastomers have been studied in detail; and long term snail control has been demonstrated in laboratory evaluations [73,79] and small scale field studies.[73,74,78-83] The mechanism of snail kill has not been elucidated, although the propensity of bis(tri-n-butyltin) oxide, "TBTO", to combine with proteinacious materials is known. Microscopic examination of moribund and dead snail tissues indicates a destruction of the cell walls in specific membranes and connective tissue, resulting in massive internal hemorrhage. TBTO and tributyltin fluoride, "TBTF", are strongly hydrophobic, and considerable evidence indicates that the solution life of these materials is extremely short with rapid absorption by suspended matter and bottom soil. Snail contact may well occur during browsing on the bottom soil or through ingestion of plants that have absorbed the toxicant.[74,79]

TBTO and TBTF are piscicidal if used at conventional dosage levels.[52] At concentration levels maintainable with controlled release materials effects upon fish seem to be minimal or absent.[74,83] A dosage range exists wherein it is possible to destroy target snails without damage to fish with TBTO and have only minor fish destruction using TBTF.[84] Although plants readily absorb TBTO, effects on vascular species are slight or non-existent under natural conditions; however, some destruction of algae has been observed.[82] Aquatic insects, amphibians, oligochaetes, daphnia and other non-target organisims do not appear to be seriously affected by the presence of organotin releasing materials.[80,83]

The environmental fate of organotins remains unknown. Tin is present in inorganic forms at 2-3 ppm in the earth's crust, and various forms of tin are found from 0.4 to 26 ppm in animal tissue.[67] Organotins, including the molluscicidal dibutyltin maleate, are metabolized by higher life forms and excreted without accumulation in tissues.[26,67] It has been shown that tin is an essential trace element in mammalian nutrition.[26] Organotins apparently accumulate in snails, but not in fish.[83,84]

Table 2 illustrates long term exposure of fish and snails to organotins and other controlled release toxicants under laboratory conditions.

Niclosamide is more piscicidal than molluscicidal and indeed is used as a trash fish toxicant and sea lamprey larvicide.[85]

Organotins are readily absorbed by suspended inorganic and organic materials.[73,87] BioMet SRM and a TBTF releasing experimental material (CBL-9B) show molluscicidal activity even when buried in mud, indicating that the adsorbed toxicant remains unaltered chemically and readily desorbs.[88] pH and dissolved ion content of natural waters also affect the rate of organotin release and probably that of snail uptake.[87,89]

TABLE 2

Effects of Ultralow Molluscicide Dosages
On Fish and Snail Life in Laboratory
Microenvironments[19,20,89,91]

Toxicant	Snail LD_{99} (30 Day)	Fish LD_0* (30 Day)
TBTO	0.006 ppm/day	0.007 ppm/day
TBTF	0.008 ppm/day	0.009 ppm/day
Niclosamide	0.100 ppm/day	0.0016 ppm/day
Trifenmorph	0.010 ppm/day	0.090 ppm/day
Cu++	0.040 ppm/day	0.170 ppm/day

*estimated from LD_{50} values. Lebistes reticulatus ("guppy") was used as the nontarget fish.

BioMet SRM may be of limited use in flowing water systems.[90] That is, one may not be able to achieve good downstream carriage--especially if molecular movement is via soil particles. Consequently a one spot treatment in an irrigation system, for example, may be useless. However, spacing of the controlled release pellets along the waterway may overcome this problem.

Various elastomers containing niclosamide have shown promising molluscicidal properties in the laboratory.[86] Field tests have not been performed save for one small evaluation in a St. Lucian marsh that failed to provide adequate control.[91] Niclosamide applied conventionally or in slow release form to mud surfaces show long term biological activity;[91] however, mud burial tests have shown poor bioassay results.[91,92] The commonly used ethanolamine salt of niclosamide is pH sensitive,[87] readily absorbed by suspended inorganic material [93,95] and detoxified by soluble minerals.[93,94,96] Suspended organic substances likewise absorb niclosamide.[96] Bacterial degradation of niclosamide has also been demonstrated.[97,98]

Incracide E51 has shown long term continuous copper ion release and biological efficacy against snails under laboratory conditions.[20, 72,99,100] Release time at efficacious levels is in excess of 6 months, and effectiveness has been predicted for a year.[74,79] Snail kill will occur through an intervening mud barrier.[88] The low copper ion concentrations held through controlled release will destroy target snail life without apparent damage to fish life.[101] In small pond tests the sinking of Incracide E-51 pellets to the mud bottom effectively destroyed bottom dwelling snails while top dwellers were unaffected.[100]

The biocidal mechanism involved with copper activity against snails is not as yet well understood, although indications point towards degeneration of the osmoregulation function in vital epithelial surfaces and/or interference with the functioning of succinic dehydrogenase.[101-103] Copper ion denatures most enzymes, nucleic acids and glycoproteins.[104]

Both organic and inorganic constituents normal to natural waters inactivate copper ion through chemical reaction and precipitation of an insoluble chemical or through bonding as a chelate.[105-107] Fulvic, humic and amino acids complex with copper.[108] It has been demonstrated that the toxicity of an organic copper compound (toward snails) is primarily dependent upon the degree of stereochemical encapsulation of the copper moiety.[109] The chronicity effect is apparent in laboratory bioassay studies[63,66,84,86,101] and confirmation is indicated by respirometer investigation.[110,111]

2. Bait Molluscicides

Another controlled release technique for destroying Schistosome host snails lies in the use of a bait. Bait materials comprise a toxic element that is not released to the external environment, an attractant that is slowly and continuously released and an insoluble binding matrix that provides integrity to the granule or pellet. Baits based upon the use of niclosamide and trifenmorph have been developed and shown to be biologically efficacious against both marine and fresh water snails under laboratory conditions.[112,113] Amphibious snail hosts of Schistosoma japonicum can be destroyed using baits whereas the conventional method of attacking these molluscs is often ineffective.[114]

Attractants used with snail baits tend to be genus specific and thus it may be possible to tailor the bait to control a host snail species without destruction of non-target snails.[112,115,116] Trifenmorph appears to be the superior toxicant; and baits containing this agent have provided good kills under field conditions with no observable effects on non-target fish, amphibians, water insects, and round worms.[115,117-119]

Copper sulfate baits have been prepared; however, snail acceptance is poor.[115] The best binders of those evaluated are the Carboset^{tm} type of polyacrylates. Snails can ingest these polymers and will do so if an attractant is present.[118] Carboset acrylics are pH sensitive and thus soluble in alkaline water. Therefore, a crosslinking agent, zinc or calcium ion is used for stability.[116,120]

Controlled release techniques, in theory, should permit intervention in the disease transmission cycle through the destruction of the larval forms of the schistosome.[62,121] Organotins were found to be effective cercariacides at extremely low dosages.[122-125] Environmental impact, if proportional to the concentration of the active agent, would be only 1/50th to 1/600th that involved in the use of conventional molluscicides.[122] Cercaria penetration of mice was prevented within a few minutes of introducing controlled release organotin pellets.[115-116] Even at organotin concentrations as low as 10-10 g/cm3 effects on cercaria and miracidia are profound.[125,126] Controlled release copper ion will supress miracidial infectivity at 0.01 ppm.[72] Organotins drastically reduce cercaria mobility, and hence penetration capability, after a few minutes exposure.[75,126]

Cercaria baits, utilizing glutamic acid or other substances as the attractant in an acrylic binder, represent another method of destroying the larval schistosome prior to human contact.[114,127] In regard to environmental contamination in the United States, however, the salient features of controlled release molluscicides clearly indicate that one can use much less chemical agent with greater safety and economy, perform the desired pest control operation, and apparently decrease environmental impact relative to the observed with conventional usage of the same toxicant. It is also seen that rate of toxicant release from the elastometric matrix can be controlled through proper compounding and the appropriate vulcanization condition.[76,128]

C. INSECTICIDES

Controlled release insecticides can be conveniently classified as larvicides and adulticides; and each category can be further considered in terms of the release technique employed. The control agent used may be a toxicant and insecticides have conventionally been substances that induce a toxic reaction in the target insect. However, the authors are including in this section agents which are not toxic, but which nevertheless can be utilized in insect control, namely, pheromone substances that alter insect behavior, IGRs (insect growth regulators) and JHMs (juvenile hormone mimics).

Various agents that destroy the larval form of the insect have been incorporated in polymers through encapsulation or other techniques. Laboratory studies on controlled release organotin formulations against mosquito larvae indicated considered merit in the use of such materials; unfortunately, due to the rapid absorption of organotins by organic water constituents, field results were poor.[129-137] Another larvicide showing long lasting effects, was Abate in an ethylene-propylene-diene terpolymer.[132-134]

During the course of this effort it was discovered that the mortality threshold for mosquito larvae was considerably lower for controlled release materials than that with the same agent applied in the conventional manner. It was thus postulated that release of the given toxicant from a rubber surface was molecular in nature and therefore unlike the molecular aggregates believed produced when extremely hydrophobic materials are added as emulsions to an infested watercourse.[129,131,133]

Juvenile hormone mimics represent a new class of agents which permit insect control through interference with the growth cycle. Such morphogenetic materials tend to be very specific in activity and usually non-toxic in the general sense. Meltzer adequately summarizes the nature of this technology and the state of the art in his text.[135] JHMs for nine insect species of economic importance have been identified.[136] A material that inhibits chitin synthesis is also known.[137] Synergistic effects are noted from combining JHMs with conventional insecticides.[138,139]

Several morphogenetic agents have been evaluated in controlled release elastomeric matrices. Altosid SR-10 formulation, manufactured and commercialized by the Zoecon Corp., is believed to be the leading material of this type.[140] Methoprene, the active agent, is incorporated in a polyurethane foam that provides a degree of protection from environmental degradation--especially insolation. Methoprene usage in the conventional sense is probably not economically feasible due to its very short environmental half-life (a few hours). Altosid SR-10 shows greater larvicidal potency than that of methoprene alone at comparable dosages.[141] The SR-10 formulation has shown excellent mosquito control under field conditions.[141-143] 100% A. aegypti kill for a 100 day test period is reported.[142] It has been said that Altosid SR-10 shows a chronicity effect.[144]

In general JHMs under evaluation are non-toxic to non-target mammalian life, easily metabolized, highly biodegradable with no toxic residues, and they exhibit very low environmental persistence.[135,145,146] There is at least one report indicating that metabolites of one JHM do affect algae.[146]

The environmental characteristics and efficacy of some of the JHMs and similar materials are highly favorable when they can be applied. However, they do have the defect of being ineffective against the larval stage, which for most insects is the one that does the damage. One area that cannot be ignored for long is that of increasing tolerance of a given species for the JHM control agent. A great increase in tolerance of Culex pipiens quinquefasciatus (Say) larvae to methoprene and hydroprene has already been demonstrated.[147] It is likely that the JHMs will be subjected to the same resistance problems as observed with more conventional xenobiotics.[148,149]

The major effort to date involving the incorporation of larvicides in non-elastomeric polymers has been performed by a group of scientists at the U. S. Army Environmental Hygiene Agency, Edgewood Arsenal, MD. Initial work involved the use of casting plaster as a binder for Abate.[150] Rapid loss of the toxicant from such briquette type dispersing systems led to the search for an improved binder. Miles and Woehst, meanwhile, demonstrated that 20 weeks of mosquito larvae control could be achieved by the use of a polyvinyl chloride/Abate formulation.[151] In this case it was noted that the agent loss rate could be increased by increasing surface area of the pellet or using a surfactant, such as Triton X-100 as an additive.

Whitlaw and Evans at USAEHA formulated Abate, Dursban (chlorpyrifos), naled and malathion in polyvinyl chloride, polyurethane foam (Isofoam PE-12) and polyamide (Elvamide series).[152] Superior larvicidal activity was noted with Abate/PVC and Dursban/PVC. The loss of Dursban from PVC was not affected by choice of plastisol used or the plasticizer, a necessary additive.[153] It is well recognized that Dursban used as the conventional emulsion destroys piscine life, has a dramatic effect on mallard ducks (42% mortality at 1 lb./acre) and reduces zooplankton populations.[154]

Dursban/polyethylene formulations were found to give greater efficacy than the PVC bound materials, and efforts since 1971 or so have focused on the use of polyethylene plastics.[155,156] Abate/PVC was also found less effective.[156]

Residue studies indicated that the long term Dursban concentration in treated waters was not proportional to the toxicant loading in the pellet, unlike Diazinon and Supracide PVC formulations where release rates increased linearly with increased loading.[157,158,159]

Both Dursban/PVC and Dursban/PE applied to artificial field pools provided 100% effective mosquito larvae control over a 22 to 24 week evaluation period, compared to a 1 to 2 week average control using

Dursban emulsion.[21,161] It was later demonstrated that a 5 ppm controlled release PE or PVC Dursban pellet would provide at least 18 months larvae control in outdoor pools.[162] Residual toxicant levels increased with higher dosage rates, increasing time at constant dosage, and increased surface to volume ratio of the pellet.[163] Chronic effects were postulated from observations that very low Dursban concentrations (0.1 to 0.23 ppb) gave higher than expected larvae mortality.[164] Residue levels vary with organic content in the treated water course.[165]

Controlled release Dursban definitely has less environmental impact than that observed in the conventional use of this agent.[166] However, since Dursban is maintained in the water course for extended intervals of time, a direct comparison with Dursban emulsion cannot be made. Evaluation of the environmental effects of controlled release Dursban/CPE formulation over many weeks indicated that benthic populations were unaffected, diatom levels dropped and Daphnia were killed. Most phyto- and zooplankters showed relatively little effect.[167] Evaluation in rice culture pools indicated that the roots absorbed Dursban but no translocation to the grain occurred.[167] In a few instances the impact of CR Dursban is greater than that observed with the use of the emulsion; e.g. suppressive effects on larval dytiscid, chaoborid, and gerrid populations.[168]

Work with PVC/fenthion and PVC/Naled has demonstrated feasibility for insect control, and such formulations may, through proper compounding, see future use.[169]

Microencapsulation is a means of applying a thin, usually solid, polymeric envelope around small solid particles, liquids or dispersions. The process dates back to the late 1930s but has only fairly recently been applied to pesticide technology.[170-172] The general merit arises from reduction in toxicity of the encapsulated material, greater stability, and ease of handling.[171]

Uses in the pharmaceutical area are widespread.[172-175] Vitamins, cathartics, stimulants, enzymes, diuretics, tranquilizers, analgesics, including aspirin, and many other encapsulated commercial agents are in use.[176] Encapsulating materials used in drug delivery systems are gelatin, polyethylene oxide, polyvinyl alcohol, ethylcellulose, cellulose acetate phthalate, carboxymethyl cellulose, various waxes, ethylene vinyl acetate and others.[172,175,176]

Food products have also been encapsulated [173,177] as well as more esoteric items such as nucleopolyhedrosis virus.[178] The expansion of interest in this area can be readily noted by observing that prior to 1960 only a few encapsulation process patents were available whereas in the 1960 to 1972 period 224 U.S. patents were issued.[173] There are essentially six basic encapsulating processes used in pharmaceutical preparations:[174] (1) Electrostatic disposition,[179] which is of minor importance, Air suspension i.e. fluidized bed,[180-182] (3) Interfacial condensation,[182-187] (4) Phase separation-coacervation,[188-192] (5) Centrifugal,[193] and (6) Spray drying. Such processes are generally applicable to pesticide encapsulation.

It is assumed that the coating substances used in pharmaceutical and food encapsulations are non-toxic and metabolized by humans and higher animals.[174,176,194]

Several other techniques are used for pesticide encapsulation which are, so far, unsuited to the medicinal trade. Polymerization techniques involve reactions of monomeric units at the interface of a core material and a continuous phase in which that material is dispersed. Speiser has, for example, polymerized a polyacrylamide skin around a toxoid.[195] Of couse various prepolymerized polymeric substances can be used as the capsule wall.[196,197] Hydrophobic polymers can be used as wall materials.[198] Of particular value is the fact that liquid pesticides can be encapsulated for greater safety in handling and dispersal.[180]

Release of encapsulated medicants appears to be by first order kinetics,[176] where the velocity constant is inversely proportional to the film thickness.[177]

It may be essential that various additives be added to the encapsulating wall material to impart desirable physical or environmental properties; a sunscreen, for instance, to retard ultraviolet deactivation of the wall or active ingredient.[178]

In recent years various concerns and agencies have investigated the feasibility of encapsulated insecticides. This is expecially true in light of the increased awareness of environmental damage arising from the overuse or injudicious use of pest control agents. Since miroencapsulation controls the bioavailability of a given toxicant, this method of application can significantly reduce associated toxicity to non-target species.[199] Agent release is controllable through various mechanisms. For instance gelatin based microcapsules containing methyl parathion show 8 day statiblity at pH 4 and an estimated 10 year life at pH 8.[200] The degree of stability of the capsule wall material can be controlled, in some instances, through the use of additiess; e.g. polysaccharide type gums in polyamide wall materials.[201]

Polyamides seem to be the preferred encapsulating material for larvicides[201,202] although polyurea[203] and various vinyl plastics and cellulosic materials have also been used.

Encapsulated Rabon has been fed to poultry and excreted mostly intact providing house fly larvae control in the manure.[204] It can be shown that much less Rabon is lost during passage through the digestive system when in the encapsulated form.[204,205] Whereas larvicidal activity is higher in the manure, as compared to non-encapsulated agent, no residues appear in egg yolk or body tissue--even at a 400 ppm dosage.[205,206] Similar results have been found using encapsulated Rabon in bovine feed to control fly larvae in manure.[207] Encapsulation protects Rabon from digestive detoxification.[208] For instance only 0.3% of a Rabon 75% W.P. will reach the feces while 15% of a 59% a.i. encapsulated form passes into the manure.[209] Later studies have shown that 6 to 9 ppm encapsulated Rabon provided 100% fly larvae control in manure while 22 to 48 ppm unencapsulated material gave 94% control.[209]

Parathion and DDT were encapsulated by Siebel, who noted not only biological efficacy in protecting domestic animals, but also that this process decreases normal repellency to the target insect. [210]

In so far as can be determined the first commercial microencapsulated methyl parathion is the Pennwalt Corporation's PENCAP M^tm to be discussed in the next section. [202, 211, 212] This material is apparently produced by the processes described in several U.S. patents.[183, 184, 186]

Pesticide encapsulation techniques have also been evaluated as a method of controlling the larval forms of the European corn borer[213] and the rice weevil.[214]

Controlled release formulations of several types have been examined as a means of controlling mature forms of insect pests. For convenience we can classify these as (1) baits, (2) contact toxicants, (3) space toxicants and (4) soil release toxicants.

1. Baits

A bait material may be of three general categories. In each case an attractant, usually nontoxic, is released, calling the pest to the location of the bait. Control is then achieved through mechanical trapping, contact with a toxic agent in or on the bait, or behavior modification.

Encapsulated mirex, using soybean oil as the attractant, has been found to provide good control of Solenopsis saevissima richteri, the imported fire ant.[215,216] Corn cob grit is used as the carrier material retaining mirex at 0.075% and the soybean attractant at 14.925% within the capsule walls.[217] Encapsulation permitted efficacious application of the bait during winter weather as well as the ability to mix with fertilizers for joint application.[218,219] Better fire ant control was achieved with the encapsulated material relative to the same dosage applied in the conventional manner.[219] In quantitative terms adequate control is achieved with 1/4 the normal amount needed, when micro-encapsulated.[220]

Mirex absorbed in wooden blocks has also been used as a termite bait.[221] Encapsulated Diazinon and Rabon in bait preparations have been successfully used for yellow jacket (Hymenoptera vespidae) abatement.[222] Without encapsulation both Diazinon and Rabon are repellent thus discouraging ingestion of the bait.

A major present thrust in bait investigation lies in the use of attractants, mainly sex attractant pheromones, to bring the insect to the vicinity of the toxicant or a mechanical trap.[223-226] A vital need in such programs has been for a method of regulating the volatile loss of the pheromone.[223] Polymeric materials were obvious candidates for evaluation. Even a simple polyethylene bag would retain and slowly release the cabbage looper pheromone by permeation.[226] Attractants and pheromones under intensive investigation are cuelure (melon fly), disparlure (Gypsy moth), gossyplure (pink bollworm), looplure (cabbage looper), methyl eugenol (oriental fruit fly), muscalure (housefly), phenethyl propionate/eugenol (Japanese beetle), trimedlure (Mediterranean fruit fly), grandlure (boll weevil), and the European elm bark beetle pheromone.[224,227,228] A complete listing of insect-behavior chemicals active in field trials has appeared recently in a volume that gives a state-of-the-art review on pest management with insect-behavior-controlling chemicals.[229] Pheromones are generally nontoxic, nonpersistent and target-specific.[224]

In gypsy moth control investigations it has been shown that the release of disparlure alone interrupts mating behavior under field conditions, thus suppressing population growth.[230,232] The problem of low field persistency was solved by the use of a controlled release device (such as powdered cork)[230,231] or a keeper that would depress volatility.[232] Encapsulated disparlure has been effectively applied to field sites.[233-236] A 94 to 97% reduction in gypsy moth mating has been achieved.[234] Methods have been developed for field application of this material.[234,237] Gelatin was used as the encapsulant.[238]

Disparlure can also be released at a slow continuous rate from laminated plastic dispensers.[239,240] Emission rate is a function of the lure concentration and laminate thickness.[239] The Hercon^{tm} dispensing material will be discussed in the next chapter.

Grandlure, the pheromone of the boll weevil has but a 1 to 2 day field life if applied by conventional means.[241] If adsorbed in some sort of matrix element, such as cigarette filters [227,242,243] or a commercial gel,[244] this life is extended to several weeks. Grandamone^{tm}, a gelled grandlure, used at 3 mg active per 1/2 x 1 3/4 x 2 inch cup provided 18 or more days of effective release in 1975 field tests involving 107,000 units.[245] Hercon dispensers loaded with grandlure have provided over 14 days release.[241,246] In a recent report from the Boll Weevil Research Laboratory[247] the Hercon dispenser caught after 12 weeks in the field 177% as many weevils as their standard dispenser--3 mg lure on a filter in a vial that had to be changed weekly throughout the test. The Hercon dispenser was not changed during the test.

Various fruit fly lures are used in conjunction with an insecticide. Trimedlure is highly volatile and possesses a short field life if applied conventionally.[248] Volatility can be decreased by the addition of various fixatives, such as pentadecanolide.[249] However, trimedlure combined with methyl parathion or malathion and encapsulated appears to be a satisfactory approach to the development of a long lasting bait.[250] Cuelure-naled combinations impregnated in fiberboard blocks have reduced melon fly populations by over 99% and show biological effectiveness for up to 7 months.[251] Culure-malathion baits with cotton string as the carrier have been successfully utilized in completely eradicating the Queensland Fruit Fly on Easter Island.[252] Cuelure-naled combinations in polyacrylic and polyisobutylene matrices look promising.[253]

Evaluation of sex attractants for the Oriental fruit moth and the lesser appleworm indicated about 4 weeks release life from encapsulated formulations.[254]

Cabbage looper pheromone has been incorporated in polyvinylchloride and a 15 month release life noted.[255] Also over 120 days emission of the lure has been provided by incorporation in a Hercon type dispenser.[256] Looplure has also been microencapsulated by the National Cash Register Company.[226]

A mixture of MCP (methylcyclohexanepropionate) and Eugenol is an attractant for the Japanese beetle. Although the chemicals have volatilities that differ markedly, they were volatilized as a vapor of constant composition by means of a dual wick device in a bottle containing the chemicals.[257] The device makes it possible to release from a trap over a prolonged time the vapor composition that is found most attractive for the target insect. Not only is the vapor composition fairly constant, but the composition of the lure in the bottle remains fairly constant.

The European Elm bark beetle pheromone is a mixture of three materials, each chemical being ineffective if used alone.[258,259] Polyethylene vials have been used as a dispenser for the lure.[260] However, superior performance has been shown when the pheromone mixture is incorporated in the Hercon^{tm} dispenser, FRL hollow fibers and a micro-capsule dispenser.[228] The Hercon system is easiest to use in the field.[261]

At this time attractant pheromones for at least 40 economically important insect species are known.[239] Systems in use against several fruit fly species and the boll weevil appear very promising, and it is anticipated that the near future will bring a number of pheromone/toxicant or pheromone/trap systems to fruition--and requests for registration.

An obvious distinction can be made between target intoxication arising from physical contact with an insecticidal powder, liquid, etc., and intoxication arising from exposure to vapors. However, in a given system either or both mechanisms may be present--and in some instances it is not clear as to which predominates. Therefore, the term "contact toxicant" as applied to various systems may be arbitrary. A number of controlled release insecticides seem to be properly classified as contact toxicants and are discussed at this point.

Feinberg has investigated the use of a number of insecticides in vinyl type paints and floor waxes as a means of destroying crawling insects.[262] A number of insecticide/polymer combinations have been evaluated against the Mahogany Shoatborer, with one material, carbofuran in Versamid 940 polyamide, showing up to 340 days longevity.[263]

Three controlled release insecticide systems have recently become commercially available, at least in regard to several specific usages. Killmastertm, an anticockroach paint containing 1% to 2% chlorpyrifos has provided excellent control for over 3 months.[264,265] Pencap M^{tm} encapsulated methyl parathion has been experimentally used for the control of gypsy moth, corn earworm, crickets, mites, boll weevil and the boll worm.[266] Probably the major advantage with encapsulated methyl parathion lies in greater handling and environmental safety rather than any dramatic increase in efficacy.[267] The Hercontm plastic insecticide dispenser incorporates chlorpyrifos, Baygon, diazinon in a 3-layer laminated polyvinyl chloride construction.[268] This product (with chlorpyrifos) is now being sold by Johnson Wax under the name "Roach Tape." The 1" x 4" tapes are judiciously placed about kitchens and bathrooms to effect control. Long term cockroach control has been demonstrated.[268,269] This material can be prepared as granules, strips, chips, confetti and so on.[270] Action appears to be contact rather than fumigant--a 2 second cockroach contact being adequate for mortality to ensue.[270] Biological effectiveness against the carpet beetle, the confused flour beetle and the rusty grain beetle has also been reported.[271] These materials will be discussed in greater detail in later sections.

A major effort keyed to the development of controlled release volatile insecticides has revolved around the use of DDVP (dichlorvos). The remarkable vapor toxicant properties of this material have made it useful in insect traps and sprays.[272] The Shell Vapona^tm dispenser (DDVP/PVC) became available in the 1960s. DDVP release from polyvinylchloride and montan wax was shown to provide sustained control of adult mosquitoes for over 10 weeks and larvae for up to 19 weeks.[273] Similar materials demonstrated efficacy against bed bugs and the oriental rat flea, but did poorly against cockroaches.[274]

DDVP release from various thermoplastic resins has been discussed, although PVC and especially Bakelite QYNV seem to be preferred.[275] Naphthalene, camphene, camphor and other nonpolymeric materials can also be used as a binding matrix--with DDVP preabsorbed on some sort of a carrier material such as colloidal silica.[276] Aries has shown that DDVP, with a proper stabilizer, can be impregnated in a cellulose fiber and long term release achieved.[277] The so called Dynachem process wherein a coevaporant is used to regulate DDVP volatility uses cellulose as the inert supporting element.[278] A stabilizer is essential to prevent DDVP hydrolysis. Materials such as butyl nicotinate and isobutyl benzoate have been used.[279] DDVP has been incorporated in carboxylated polyacrylates[280], polyethylene, polypropylene, polystyrene, polyesters and other polymers, and caused to release at a useful rate through the coevaporant method.[281] Anhydrous cellulose seems to be the preferred base, however.[282,283] One invention describes a cellulose paper impregnated with DDVP and then coated with polyethylene.[284] Rabussier and Mandon have formulated DDVP in olefin polymers, especially epoxies, and demonstrated that slow release occurs.[285]

Bogaard has adsorbed DDVP on various granulated hydrates, such as gypsum, and upon addition to a paraffin and polyethylene base, a long lasting controlled release insecticide dispenser was produced.[286] This is based upon the solid deodorant system advanced by Nysted.[287]

While the majority of the developmental effort has been concerned with the use of DDVP released from a solid matrix, other investigators indicate alternate routes to the same end. Soloway and Morales have shown that thiono-DDVP is superior to DDVP in insecticidal potential and can be incorporated in a plastic matrix.[288] Others have shown that DDVP can be chemically bound to higher alcohols or organic acids, incorporated in a dispensing system. Fumigation action is created by the gradual release of the appended DDVP molecule.[289]

Agricultural insecticides usually act in soil via solution in ground moisture and consequent insect contact, and upon the surface of the ground or on vegetation by contact. A few display fumigant action in soil. Very little effort has been devoted to the development of non-persistent controlled release agricultural insecticides, excepting the Pencap Mtm encapsulated system. Of course a number of materials developed for mosquito control etc. have been subjected to a secondary evaluation against crop pests.

Pirimicarb, an aphicide, has been adsorbed on a pumice carrier and coated with a short oil rosin-resin-wax mix to modify release.[290] Efficacious results were noted. In another noteworthy advance it was demonstrated that the field lifetime of aldicarb could be dramatically increased by absorbing it on charcoal and adding an insoluble binder.[291] Efficacy against cotton insects was shown; also, such compositions did less damage to the treated plant.[292] Cellulose acetate appeared to be the superior binding element.[293] It was shown that this system follows first order kinetics in terms of release rate and also that the release is inversely proportional to the percent binder used.[294]

It has been demonstrated that a number of insecticides can be added directly to a monomeric mix and then *in situ* polymerization initiated; the end result is that the agent is dispersed in the resulting polymer.[295,296] Another approach is to incorporate the agent in waste products. Various carbamates and organophosphates can be adsorbed on wood chips and coated with wax to provide a slow release mechanism.[297] Allan et. al. have discussed this concept and advanced the design of such systems.[298] The idea of absorbing or adsorbing the pest control agent on some sort of carrier and then coating with a polymeric film former has been advocated many times, but relatively little practical work has gone into the development of useful products based upon this scheme.[299]

Sjogren has used castorwax and a silicate in a controlled release dimilin formulation.[300] The castorwax hydrolyzes to ricinoleic acid and glycerol in natural surroundings. Both substances should have no environmental impact and the agent (a chitin synthesis inhibitor) has a very short field life.

Various insecticides appear to be incorporable in controlled release matrices; the phenylureas and tricyclohexyltin hydroxides for instance.[301,302] Elastomer insoluble pesticides can probably be rendered soluble by the method described by McCoy and Swanson, and thus become incorporable in a diffusion-dissolution type matrix.[303]

D. HERBICIDES

In this section, controlled release agents used against aquatic and terrestrial vascular plants are described. Bactericides, algicides and fungicides are covered in later chapters. For convenience CR herbicides can be categorized as aquatic/plastic, aquatic/elastomeric and agricultural.

During the period 1968-1970 scientific personnel at the U.S. Army Environmental Hygiene Agency demonstrated that the aquatic herbicides endothall, dichlobenil, 2,4-D acid esters, 2,4,5-T acid esters and silvex acid esters could be incorporated in vinyl and polyamide resins.[304,305] The preferred polyvinyl chloride carrier was made of Geon 135 plastisol.[305] Whether 2,4-D release from PVC was superior to 2,4-D/attaclay granular formulations was a moot question.[306,307] Probably a superior approach lies in using polyethylene as the matrix material.[308] Fenac acid in either polyethylene or polyvinylchloride provided long term control of Eurasian watermilfoil.[309] Fenac residues from Fenac/PVC were detected for 46 weeks.[310]

Harris et.al. in his work with Fenac/polyethylene provided irrefutable experimental evidence that long term controlled herbicide release from plastic matrices was technically feasible. He showed that release rate was proportional to pellet porosity; and it is well known that porosity is controllable by varying the thermal history of the material or adding a filler, such as sucrose, that will enhance pore structure.[311] Harris further demonstrated that when diffusion is the rate controlling factor, toxicant loss is proportional to $\sqrt{\text{time}}$, i.e. the general Higuchi equation holds; whereas if dissolution (surface resistance) is rate controlling the system follows first order kinetics.[312]

Harris and his colleagues in more recent endeavors have polymerized vinyl monomers containing hydrolyzable herbicidal moieties as pendent side chains.[313] Both 2,4-D and silvex were so incorporated.[314] Other monomers, such as the acryloyloxyethyl esters of 2,4-D, could also be used as starting materials.[315] Release rates tend to be slow but can be increased by incorporation of hydrophilic groups along the polymeric carbon backbone.[316]

Alkyd resins can be used in a similar fashion. For instance glycerol, phthalic anhydride, and 2,4-D acid can be polymerized to form a herbicidal resin.[317]

In work sponsored by the U.S. Army Corps of Engineers the butoxyethanol ester of 2,4-dichlorophenoxyacetic acid (2,4-D BEE) was incorporated in various natural rubber based compounds and efficacious herbicide release demonstrated.[310,318] 2,4-D BEE/natural rubber materials could be made as sinking pellets, floating pellets or suspending strands; the herbicide is released in the phytozone of interest, thus minimizing general environmental contamination.[319,320] Laboratory evidence showing the tendency of 2,4-D to "layer out" in still water was presented.[319]

Outdoor pool tests demonstrated that 2,4-D BEE/natural rubber formulations showed long term release with control of water hyacinth and Eurasian watermilfoil.[309] Such formulations are said to be nontoxic to fish.[309]

During the course of this work the chronicity phenomenon was discovered and verified for several herbicide/weed interactions.[15,17,18, 321]

The natural rubber compounds appear superior to polyvinylchloride-based materials for field work.[322-3] In the first small scale field tests of compound 14ACE-B, excellent control results were observed with water hyacinth and watermilfoil.[321] In the 1/2 acre hyacinth test site it required 7 months for complete elimination of the target plant; however, no reinfestation has appeared at two years post treatment.

The controlled release copper molluscicide, Incracide^{tm} E-51, will destroy specific vascular aquatic weeds, Vallisneria americana, Cabomba caroliniana and Lemna major (duckweed) at concentrations as low as 1 ppm.[324] Normally copper sulfate is not used against these pests due to the very high dosage requirement in the conventional sense. Thus it might be feasible to replace more persistent organic aquatic herbicides with such materials.

Diquat, silvex, endothall, fenuron and 2,4-D acid have also been incorporated in a number of controlled release elastomers and will release at efficacious levels for prolonged time periods.[325]

Relatively little effort has been expended to date in the development and evaluation of practical CR agricultural herbicides. The cause of this situation is unknown. A number of well known scientists have discussed the concepts involved and the advantages to be gained. Dr. G. Graham Allan and his colleagues at the University of Washington assert that 150 days of controlled release would reduce the amount of pesticide used by a factor of 1000 to 8.[326] Himel has pointed out the great waste of chemical agents arising from conventional application methods, claiming that a 75 to 90% reduction in quantity is feasible.[327] Collins, among others, has developed the mathematical concepts for translocation of herbicides and insecticides from controlled release microgranules and microcapsules through soil to the target organism.[328] Diffusion coefficients of various herbicides in soil, and effects of moisture and soil type on rates are known or can be determined.[329] Hilton has predicted a bright future for controlled release herbicides.[330] Based upon the obvious success of controlled release formulation in the antifouling and molluscicide area, and demonstration of the feasibility of CR insecticides and aquatic herbicides, one of the authors (NFC) has urged the extension of this technology to agricultural herbicides.[331]

Allen et.al. have developed a mathematical controlled release model system wherein waste products, such as tree bark and lignin are used as the binding polymers.[332,333] A number of herbicides, including 2,4-D, 2,4,5-T, 2,4-DB, MCPA, TCA, dalapon, silvex and others, can be combined with forestry wastes by esterification.[334] Selective phytotoxicity was developed using 2,4-DB and Douglas fir bark. The polymer created releases 2,4-DB slowly enough that plant absorption occurs before 2,4-DB is enzymatically degraded to 2,4-D which is toxic to non-target species. In this instance red alder seedlings are eradicated while Douglas fir seedlings are not affected.[335] The concepts advanced by Allan and his coworkers involve a dramatic reduction in total herbicide usage and completely degradable natural products as polymer bases--and the technique is proven in field work. So far the scientific community has apparently ignored the implications of this work.[336]

Beasley and Collins have purportedly polymerized 2,4-D, using iron nitrate, into a polymer that slowly decomposed releasing the 2,4-D moiety.[337,338] One author (NFC) was not able to confirm this polymerization technique.[319] Sinclair has shown that 2,4-D can be incorporated in a biodegradable polylactic acid and controlled release over a several month period maintained.[339] Others have shown that 2,4-D esters of starches will release 2,4-D by glucoside bond cleavage upon hydrolysis.[340] Water decomposable urea polymers may also be used as binding elements for various herbicides.[341]

Dicamba, dichlobenil, DNBP and other agricultural herbicides are incorporable in various waxes and resins and will, purportedly, release in the soil.[342] Thiazine type herbicides can be formulated in various elastomers and caused to release upon exposure to moisture.[343] Monomers containing terrestrial herbicides as pendant substituents have been synthesized and polymerized.[334] 14ACE-B aquatic controlled release 2,4-D BEE herbicide formulation buried in soil suppressed the growth of mustard (Brasscia sp.) for six weeks.[345]

E. FUNGICIDES

Little effort has been devoted to the development of controlled release fungicides. Geary has shown that fungicides such as captan can be impregnated in various inert carriers (mica, kaolin, etc.) and then coated by polymerizing a urea formaldehyde film around the carrier.[346] Inherently fungicidal resins, for paint use, can be made by the polycondensation reaction of glycol + chlorophenol ester + benzenecarboxylic acid.[347] Various low molecular weight polyisonitriles are likewise inherently fungicidal.[348] Fungicidal groups can be chemically bound to various plastics by ion exchange reactions.[349] Fungicides have been used as rubber latex additives for protective seed coatings.[350] Benlate can be encapsulated on onion and other seeds to provide protection against fungi attack until germination.[351]

The aforementioned fungicide/polymer formulations do not fall within the controlled release category although the principles involved and the feasibility demonstrated may be germane to future developments. In perhaps more pertinent work it has been shown that antifouling rubber will release organotins at levels sufficient to destroy Hermodendrum cladosporum fungi in a dynamic potable water reclamation system.[352] Cardarelli has also demonstrated that tributyltin fluoride and other organotin vapors released at room temperatures from various elastomers will destroy pathogenic fungi over at least an 18 inch air gap under conditions of moderate ventilation.[353]

F. RODENTICIDES

The bait approach to rodent control is historically quite old. One basic problem lies in the ability of the rodent often to detect the presence of the toxicant and thus reject the bait. Encapsulation of the agent, usually an anticoagulant, has led to enhancement of bait acceptance. This has been observed with norbormide,[354] Alphachloralose,[354] and warfarin.[355,356] Encapsulation masks the bitter taste of norbormide.[357] Abrams and Hinkes reported that unencapsulated warfarin baits have a 3% to 9% rat acceptance while encapsulation raised the acceptance level to over 30%.[356] However, Cornwall has pointed out that while encapsulation improves rodent intake it does not increase kill--possibly due to detoxification processes being sufficient to overcome the much slower release rate.[358]

G. NEMATICIDES

Ethoprop (O-ethyl S,S-dipropyl phosphorodithioate) has been incorporated in natural rubber and an ethylene-propylene-diene terpolymer.[359] A 3 month release life is possible. Also DBCP (1,2-dibromo-3-chloropropane) has been encapsulated with a water sensitive, biodegradable wall material.[360] Hopefully this technique would extend DBCP through a dry period until soil moisture is available to rupture the capsule membrane.

The basic problem overwhelming known attempts to create a controlled release nematicide arises from the very low boiling point of the 15 to 17 fumigants in use. This factor negates processing via press cures of elastomers or hot melt extrusion of plastics.

H. ALGICIDES

Various copper compounds have long been used as algicides in reservoirs, swimming pools, farm ponds and elsewhere. Copper ion, although easily precipitated by combination with carbonates and other natural water constituents, appears to be as toxic to algae in the insoluble form as in the ionic.[361] Copper solubility does limit fish toxicity however.[111] Copper sulfate, probably the most popular algicide, loses some effectiveness in alkaline waters while Cutrine (copper sulfate-copper triethanolamine) is about equally effective regardless of pH.[362]

Silver compounds, mercuric chloride, phenyl mercuric acetate, and various quaternary ammonium chemicals have also been used as algicides. Many such materials appear to be biodegraded (and detoxified) by the algae.[363]

As in other areas copper salts and other algicides last but a few days in water so that periodic retreatment is necessary.[364] Consequently the use of controlled release materials--if the overall dosage added to the environment is not greater than with conventional treatment--is indicated. The Incracide E-51 controlled release copper sulfate monohydrate material is active against some types of single celled algae and at least several filamentous forms.[324] Experimental copper releasing thermoplastic materials have been recently produced and release copper ion for several months.[365,366] Predictably an increase in effort on research and development of controlled release algicides will be forthcoming.

I. PREDACIDES

The use of controlled release devices against marauding predacious animals may be of future concern. Control of predators such as the coyote, which prey upon man's domestic animals, is an important economic problem of the sheep raising industry. Normal control methods, such as poisoning, tend to be not only environmentally hazardous but counterproductive in that nonpredators are more likely to be poisoned.

Toxicant delivery systems keyed only to release upon the act of predation is an approach of some merit. The concept of sheep collars containing sodium or potassium cyanide encased or encapsulated in a protective membrane that ruptures upon the act of attack has been evaluated and shows some promise in pen tests.[367,368]

J. REPELLENTS

Repellent substances such as indalone and diethyl-m-toluamide ("DEET") can be incorporated in film forming sprayable polymeric materials similar to those discussed in U.S. Patent 3749772.[369] Conrady and Stockman reported on such compositions keyed to human topical use.[370]

Polymers greatly retard the volatile loss of repellents so that one may in certain circumstances appreciably extend the biologically active life of a given dosage. One of the authors (NFC) has formulated simple sprayable compounds of DEET in polyacrylics and polyurethanes and achieved several months release on window screening and other inert substances. Unformulated DEET lasts but a few days in sunlight, to several weeks in shade.

K. FERTILIZERS AND PLANT NUTRIENTS

Although not directly related to the thrust of this project, controlled release fertilizers have been developed, and the techniques and materials used will be applicable to the pesticide area of concern. Therefore, a review of the progress made with such materials is not beyond the scope of this report. It is well known that the present and potential environmental contamination arising from the mass use of fertilizing materials and plant nutrients is substantial. It may well be that this problem area is greater than that arising from pesticide use--especially with the removal of the very persistent chlorinated type pest control agents. Since controlled release techniques applied to fertilizer use at least promise amelioration of the environmental impact, it may be noteworthy to consider such materials of more than just indirect relevance to this endeavor.

Hayes et.al. showed certain advantages in the use of ureaforms as an insoluble nitrogen source.[371] Slowing down the rate of available nitrogen leads to improved agricultural yield. In 1966 Stansbury et. al. demonstrated that ammonium sulfate could be incorporated in an asphalt/wax coating by preparing a hot melt, extruding, cooling and pelletizing.[372] Later Lunt described the Thiokol technique for coating urea granules with sulfur and a plasticizing agent--and then using a wax sealer.[373] It was shown that one application of this controlled release urea was equivalent in crop performance to three applications of urea in the conventional sense. Rindt et. al. reported a dissolution rate for such material as 0.2%/day--compared to 100%/day for noncoated urea. It is noted that such formulations need certain additives such as a microbiocide, for example sodium pentachlorophenate, and conditioning agent (kaolin, vermiculite, etc.) to eliminate tackiness.[374] Economic and other advantages have been noted.[375-377]

Of course the controlled release of nitrogen can be achieved by using slowly hydrolyzing chemicals, such as 1,1-diureido isobutant (IBDU). The disadvantage seems to be the relatively high cost.[378] Coated ureas are undoubtedly a major advance in fertilizer application since they require only one treatment per season; IBDU even shows a residual carryover to the next growing season.[379-380]

Sulfur coated urea, potassium chloride and phosphate have been used for some time in agriculture and horticulture. Superior performance due to the controlled release characteristics has been reported.[381-383]

In general, available controlled release materials are more efficient, less costly to apply, and they reduce the burning hazard associated with conventional materials.[384] However, the available materials are largely based on the use of sulfur or another coating material, or on the use of a relatively insoluble material that slowly changes chemically to a soluble one utilizable as a fertilizer or growth regulator.[378,385,386] Other release mechanisms can be considered experimental. Cap-cyc^{tm}, an encapsulated chlormequat growth regulator (Minnesota Mining & Manufacturing Co.) is an exception, but so far use has been confined to horticulture.[387-389]

Fertilizers and micronutrients for trees have been commercialized wherein the agent is packaged in polyethylene or other slightly permeable plastic film bags apparently with good results.[390]

To our knowledge hot melt materials wherein an intergral polymer/fertilizer mix is produced have not reached the marketplace. Insecticides and nematicides can be directly incorporated in such formulations offering a distinct advantage.[391]

The Sommer et. al. patent is particularly intriguing. In this instance the plant nutrients are dispersed in a hydrophobic matrix and hot melt extruded as a cylinder. The cylinder is then coated with a water insoluble, impermeable wax or other substance--leaving one or both ends uncoated. The "open" end then will slowly release the soluble nutrient as ground water penetration occurs. Shell Chemical Co.[392]

L. MISCELLANEOUS

Controlled-release bactericides of several types have been developed. Cardarelli and Major have shown that various organotin containing elastomers will release sufficient toxicant to destroy _S_. _albus_, _S_. _pyrogenes_, _E_. _coli_, _A_. _faecalis_, _P_. _vulgaris_, and _B_. _subtilis_ in potable water systems and in urine.[352] Germicidal properties can be conferred on plastic and elastomeric films through the ion attachment of streptomycin, colimycin, etc.[349] Polyvinyl chloride can be impregnated with bis (tri-n-akyltin) sulfosalicylates a long-term bactericidal property established.[393-395]

Urea-formaldehyde polymers containing Sevin, dimethoate, lindane and other toxicants can be fed to cattle to control internal parasites.[396] Likewise various organophosphorus toxicants can be incorporated in polyvinyl chloride or polyvinylidene chloride and used as an anthelmintic and for larvae control in manure.[397] Proper formulation, for instance, will allow the anthelmintic to pass through the rumen, reticulum and omasum of bovines without loss of agent--and then release in the abomasum and intestine.

III. AGENTS UTILIZED IN CONTROLLED RELEASE MATERIALS

A compendium of toxicants and other agents used in Controlled Release Pesticidal Materials is provided in Table 3. The purpose is to illustrate the rather wide variety of materials that have been investigated for this use. Trade or trivial names are given, along with the chemical name, a reference number from the E.P.A. document, Acceptable Common Names and Chemical Names for Ingredient Statement on Pesticide Labels (3rd. ed., 1975), a manufacturer's code and the more pertinent references provided in this report. A number of common items, such as ammonium sulfate, having numerous producers, carry no manufacturer or source code.

Table 3

Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
1. ABATE	0,0,0',0'-tetramethyl 0,0'-thiodi-p-phenylene phosphorothioate	845	1	132, 133 151
2. ALDICARB (Temik)	2-methyl-2-(methylthio) propionaldehyde 0-(methylcarbamoyl) oxime	11A	2	291, 293 294
3. ALDRIN	Hexachlorohexahydro-endo, exo-dimethanonaphthalene	12	7	295
4. ALLETHRIN	Allyl homolog of cinerin I; dl-2-allyl-4-hydroxy-3-methyl-2-cyclopentene-1-one	25	6	262
5. ALPHA CHLORALOSE	glucochloralose	876AA		354
6. ALPHA CHLOROHYDRIN	---	214A	---	357
7. ALPHA CUBEBENE	---	---	19	398
8. ALTOSID	(see Methoprene)	---	3	141, 142
9. AMATROLE	3-amino-5-trizole	40	4	341
10. AMMONIUM SULFATE	---	48	---	372

	Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
11.	ATRAZINE	2-chloro-4-(ethylamino)-6-(isopropylamino)-5-triazine	63	5	341
12.	BAYGON	o-isopropoxyphenyl methylcarbamate	508	8	268,270
13.	BAYTEX	0,0-dimethyl 0-(4-(methylthio)-m-tolyl) phosphorothioate	456F	8	160
14.	BENLATE (Benomyl)	Methyl-1-(butylcarbamoyl)-2-benzimidazole carbamate	75A	11	169,207
15.	BH	Benzene hexachloride	78,79	9	252
16.	BIORESMETHRIN	(±)-cis,trans-(5-benzyl-3-furyl)-methyl-2,2-dimethyl-3-(2-methylpropenyl) cyclopropane carboxylate	83E	12	295
17.		bis(tri-n-butyltin) sulfosalicylate	102C	10	269
18.	CAPTAN	N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide	159	13	393,395
19.	CARBOFURAN	2,3,-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate	160A	6	346
20.	CHLORDANE	Octachloro-4,7-methanotetrahydroindane	174	14	263
21.	CHLORMEQUAT (CYOCEL)	2-chloroethyltrimethylammonium chloride	191	1	129 262,295
22.	CHLOROPHACINONE	2-(α-p-chlorophenyl-α-phenylacetyl)-indane-1,3-dione	211C	17	387,389

Trade or Trivial Name		Chemical Name	EPA Ref.	Man. Code	Reference
23.	CHLORPYRIFOS (Dursban)	0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate	219AA	15	132
24.	CODLELURE	(E,E)-8,10-dodecadienol	---	16	400
25.		Copper sulfate monohydrate	257	18	324
26.		Crotonylidene diurea	---	---	384
27.	CUELURE	4-(p-hydroxyphenyl)-2-butanone acetate	---	20	224
28.		Cuprous oxide	266	---	38
29.	CUTRINE	Copper triethanolamine Complex	235C	21	362
30.	DALAPON	2,2-dichloropropionic acid	273A	15	334,341
31.	2,4-DB (Butyrac)	4-(2,4-dichlorophenoxy) butyric acid	316	4	336,334 335
32.	DBCP (Nemagon)	1,2-dibromo-3-chloropropane	287	15	360
33.	DDE	Dichlorodiphenyl-dichloroethane	307	---	200
34.	DDT	Dichlorodiphenyl-trichloroethane	308	---	210,295 297
35.	DEET	N,N-diethyl-m-toluamide	346	22	370
36.		Diammonium phosphate	---	---	382,384
37.	DIAZINON	0,0-diethyl 0-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate	342	5	222,262 268

Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
38. DIBROM (Naled)	1,2-dibromo-2,2-dichloroethyl dimethyl phosphate	586	13	129,169 251,253 262,397
39. DICAMBA (Banvel D)	3-methoxy-3,6-dichlorobenzoic acid	295	14	338,342
40. 2,4-D ACID	2,4-dichlorophenoxyacetic acid	315	15	297,304 309,317 34,341 344
41. 2,4-D BE	n-butylester of 2,4-dichlorophenoxyacetic acid	315AL	15	304
42. 2,4-D BEE	Butoxyethanol ester of 2,4-dichlorophenoxyacetic acid	316A	4	305,309 310,323 345
43. 2,4-D Na	Sodium salt of 2,4-dichlorophenoxyacetic acid	315D	15	339
44. 2,4-D polymer	Polymerized 2,4-dichlorophenoxyacetic acid	---	---	338,340
45. DICHLOBENIL (Casoron)	2,6-dichlorobenzonitrile	297	23	305,342
46. DICHLORVOS (DDVP)	2,2-dichlorovinyl dimethyl phosphate	328	7	273,277 278,373 284,285 286,289
47. DIELDRIN	Hexachloroepoxyoctahydro-endo,exo-dimethanonaphthalene (85%)	333	7	262
48. DIMETHOATE (Cygon)	O,O-Dimethyl S-(N-methylcarbamoyl) methyl phosphorodithioate	358	1	393
49. DIMILIN (TH 6040)	1-(4-chlorophenyl)-3-2,6-difluorobenzoyl)-urea	---	23	143

Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
50. DNBP	2,4-dinitro-6-sec-butylphenol	388A	15	342
51. DIPHACINONE (Diphacin)	2-diphenylacetyl-1,3-indandione	394	14	399
52. DIPTEREX (Chlorophos)	dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate	395	8	295,396
53. DIQUAT	6,7-dihydrodipyrido (1:2-a:2, 1-c)-pyrazidinium dibromide	402	13	15
54. DISPARLURE	cis-7,8-epoxy-2-methyloctadecane	---	16	226,230 232
55. DISYSTON (Disulfoton)	0,0-diethyl S-(2-(ethylthio)ethyl) phosphorodithioate	341	8	355
56. 2,4-D ALKANOLAMINE	Alkanolamine salt of 2,4-dichlorophenoxyacetic acid	315E	15	310,323
57. ENDOTHALL	7-oxabicyclo (2.2.1) heptane-2,3-dicarboxylic acid	421	24	305,341
58. ETHOPROP (Mocap)	0-ethyl S, S-dipropyl phosphorodithioate	434C	26	356
59. ETHREL	2-chloroethylphosphonic acid	426A	---	386
60. EUGENOL	4-allyl-2-methoxyphenol	---	27	257
61. FENAC	2,3,6-trichlorophenyl acetic acid	882	4	308,309
62. FENURON	3-phenyl-1,1-dimethylthiourea	457	25	310,341

Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
63. GRANDLURE	4 components: I. (+)-cis-2-isopropenyl-1-methyl-cyclobutane ethanol II. (Z)-3,3-dimethyl-Δ 1,B cyclohexane ethanol III. (Z)-3,3-dimethyl-Δ 1,a cyclohexaneacetaldehyde IV. (E)-3,3-dimethyl-Δ 1,a cyclohexaneacetaldehyde	---	16	245
64. HEXACHLOROPHENE	2'-methylene bis(3,4,6-trichlorophenol)	566	29	395
65. HEXALURE	(Z)-7-hexadecen-1-ol acetate	---	16	214
66. HMPT	hexamethylphosphoric triamide	---	---	332
67. IBDU	isobutylidene diurea	---	31	373, 378, 380, 384
68. KEPONE	decachloro-octahydro-1,3,4-methano-2H-cyclobuta(cd)-pentalene-2-one	275	25	262
69. LINDANE	benzene hexachloride (gamma isomer)	527	30	262, 396
70. LOOPLURE	(Z)-7-dodecenyl acetate	---	16	224, 255
71. MALATHION	O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate	535	1	261
72. MCP	methylcyclohexanepropionate	---	28	257
73. MCPA	2-methyl-4-chlorophenoxyacetic acid	557C	9	334, 341

	Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
74.	MCPB	4-(2-methyl-4-chlorophenoxy) butyric acid	558	4	334
75.	MEDLURE	sec-butyl 4-chloro-2-methyl cyclohexane-carboxylate	---	---	248
76.	MERCURIN CHLORIDE	---	544	---	395
77.	METHOMYL (Lannate)	S-methyl-N-[(methylcarbamoyl)oxy] thioacetimidate	549C	11	263
78.	METHOPRENE (Altosid)	isopropyl (E,E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate	---	3	141, 142
79.		4-methyl-3-heptanol	---	---	398
80.		methyl nonyl ketone	5730	33	271
81.	METHYL EUGENOL	4-allyl-1,2-dimethoxybenzene	---	35	224, 248
82.	METHYL PARATHION	O,O-dimethyl O-p-nitrophenyl phosphorothioate	372	34	267, 296
83.	MIREX	dodecachlorooctahydro-1,3,4-methano-2H-cyclobuta(cd) pentalene	411	25	218
84.	MULTISTRIATIN	---	---	19	258, 259
85.	MUSCALURE	(Z)-9-tricosene	---	16	224
86.	NICLOSAMIDE (Bayluscide)	Ethanolamine salt of 2,5-dichloro-4'-nitrosalicylanilide	314	8	59, 133
87.	NORBORMIDE	5-(a-hydroxy-a-2-pyridyl benzyl)-7-(a-2-pyridyl benzylidene)-5-norbornene-2,3-dicarboximide	606	38	354, 357

	Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
88.		10',10-oxybisphenoxarsine	626	15	395
89.		paraformaldehyde	633	37	395
90.	PARATHION	0,0-diethyl 0-p-nitrophenyl phosphorothioate	637	1	210, 296
91.		Pentachlorophenol	641	34	42
92.		Phenethyl propionate	---	---	224
93.		Phenothiazine	---	36	396
94.		Phenylmercury oleate	657J	---	133
95.		1-(2,6-dichlorobenzoyl)-3-phenylurea	---	---	301
96.	PICLORAM	4-amino-3,5,6-trichloropicolinic acid	39	15	338
97.	PIRIMIPHOS (Primicid)	diethylamino-6-methylpyrimidin-4-yl diethyl phosphorothionate	334A 334B	40	214
98.	PIRIMICARB (Pirimor)	6-dimethyl-2-dimethylamino-4-pyrimidinyl dimethylcarbamate	359C	40	290
99.		Potassium chloride	686	---	382
100.	RABON (Gardona)	2-chloro-1-(2,4,5-trichlorophenyl) vinyl dimethylphosphate	217A	7	207, 222
101.	SEVIN (carbaryl)	1-naphthyl N-methylcarbamate	160	2	396
102.	SILVEX ACID	(2,4,5-trichlorophenoxy) propionic acid	739	15	304

Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
103. SILVEX ESTER	propylene glycol butyl ester of Silvex Acid	739M	15	15, 313
104.	Sodium cyanide	758	32	334, 338
105. SUPRACIDE	0,0-dimethyl S-(2-methoxy-1,3,4-thiadiazol-5-(4H)-onyl-(4)-methyl)-dithiophosphate	378B	5	159
106. 2,4-5 T	2,4,5-trichlorophenoxy-acetoc acid	881	9	304, 334
107. 2,4-5 T (POLYMERIZED)		---	---	338
108. TBLA	tributyllead acetate	---	---	41
109. TBTA	tributyltin acetate	867	10	35, 53, 130, 352, 353
110. TBTAd	tributyltin adipate	---	10	131, 352
111. TBTCl	tributyltin chloride	867A	10	129, 352
112. TBTF	tributyltin fluoride	867C	10	36, 129, 352, 353
113. TBTM (POLYMER)	poly(tributyltin methacrylate/methylmethacrylate)	---	---	44
114. TBTM/TPT (POLYMER)	poly(tributyltin/triphenyltin/methylmethacrylate)	---	---	44
115. TBTN	tri-n-butyltin neodecanoate	867G	10	395
116. TBTO	bis(tri-n-butyltin) oxide	101	10	36, 129, 352
117. TBTR	tributyltin resinate	867H	10	352
118. TBTS	tributyltin sulfide	---	10	130, 258
119. TCA	trichloroacetic acid	870	15	317, 334
120. TCPN	tetrachloroisophthalonitrile	215B	---	65

Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
121. TERRAMYCIN	---	628	---	396
122. THIMET (Phorate)	0,0-diethyl S-(ethylthio)methyl phosphorodithioate	660	1	346
123. THIONO-DDVP	0-(2,2-dichlorovinyl) 0,0-dimethyl phosphorothioate	---	7	288
124. TPLA	triphenyllead acetate	896B	5	37, 133
125. TPTA	triphenyltin acetate	896C	10	54
126. TPTC	triphenyltin chloride	896D	10	54
127. TRICAMBA	3,5,6-trichloro-o-anisic acid	869	14	341
128. TRIAZINE	2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine	---	5	343
129.	Tricyclobutyltin hydroxide	---	10	---
130.	Triethyltin hydroxide	---	10	42
131. PLICTRAN	Tricyclohexyltin hydroxide	884A	10	302
132. TRIFENMORPH (Frescon)	N-tritylmorpholine	898A	7	119
133. TRIMEDLURE	tert-butyl 4-chloro-2-methyl-cyclohexane carboxylate	---	---	224, 248
134.	Triuret	---	---	375
135.	Tributyltin acrylate	---	10	46
136. URAMITE	urea-formaldehyde polymer	---	---	379
137.	Urea	902	---	374, 379 382

Trade or Trivial Name	Chemical Name	EPA Ref.	Man. Code	Reference
138. WARFARIN	3-(α-acetonylbenzyl)- 4-hydroxy-coumarin	903	14	355, 356 358
139.	Zinc oxide	920	---	386
140.	Zinc phosphide	922	30	358

Man. Code	Basic Producers
1.	American Cyanamid Co. Agricultural Division Princeton, New Jersey 08540
2.	Union Carbide Corp. Agricultural Products P. O. Box 1906 Salinas, California 93901
3.	Zoecon Corp. 975 California Avenue Palo Alto, California 94304
4.	Amchem Products Co. Ambler, PA 19002
5.	Geigy Agricultural Chemicals, Inc. Ardsley, New York 10502
6.	FMC Corp. Niagara Chemicals Div. 100 Niagara Street Middleport, New York 14105
7.	Shell Chemical Co. Agricultural Div. 2401 Crow Canyon Rd. San Ramon, California 94583
8.	Chemagro Corp. P.O. Box 4913 Kansas City, MO 64120
9.	M & T Chemicals, Inc. Rahway, New Jersey 07065

Man. Code	Basic Producers
10.	E. I. duPont de Nemours & Co. 900 Wilson Rd. Wilmington, Del. 19803
11.	Chevron Chemical Co. Ortho Division 940 Hensley Street Richmond, California 94801
12.	Dow Chemical Co. Midland, MI 48640
13.	Story Chemical Co. Farchan Div. 4702 E. 355 St. Willoughby, Ohio 44094
14.	Chempar Chemicals, Inc. 260 Madison Ave. New York, N.Y. 10002
15.	Chemical Samples Co. P. O. Box 20305 Columbus, Ohio 43220
16.	Food Industries, Ltd. Bromborough Port New Ferry, Wirral, Cheshire ENGLAND
17.	Applied Biochemists, Inc. P.O. Box 25 Mequon, Wisconsin 53092
18.	Hercules, Inc. Wilmington, Del. 19899
19.	Thompson-Harvard Chemical Co. P.O. Box 768 Kansas City, MO 64141
20.	Pennwalt Chemical Corp. 2901 Taylor Way Tacoma, WA 98401

Man. Code	Basic Producers
21.	Allied Chemical Corp. Agricultural Div. Morristown, New Jersey 07960
22.	Mobile Chemical Co. Industrial Chemicals Div. 401 East Main St. Richmond, VA 23208
23.	Gentry International Co. Flavor & Fragrance Div. 17-01 Nevins Rd. Fair Lawn, N. J. 07410
24.	BASF-Wyandotte Corp. Parsippany, N. J. 07054
25.	Nationwide Chemical Corp. P.O. Box 775 Fort Myers, Fla. 33901
26.	Hooker Chemical Co. Niagara Falls, New York 14302
27.	Swift Chemical Co. 111 West Jackson Blvd. Chicago, IL 18865
28.	J. G. Baker Chemical Co. 222 Red School Lane Phillipsburg, N.J. 08865
29.	McLaughlin Gormley King Co. 8810 Tenth Ave., N. Minneapolis, Minn. 55427
30.	Monsanto Chemical Co. 800 N. Lindbergh Blvd. St. Louis, MO 63166
31.	Universal Oil Products, Inc. Chemical Div. State Highway 17 East Rutherford, N.J. 07073

Man. Code	Basic Producers
32.	Atomic Basic Chemicals Corp. P. O. Box 146 Eighty Four, PA 15330
33.	Celanese Chemical Co. 1211-A Ave. of Americas New York, New York 10036
34.	Johnson & Johnson Co. Tavolek Laboratories Div. Fort Washington, PA 19034
35.	ICI Plant Protection Ltd. Fernhurst, Haslemere, Surrey ENGLAND

IV. MATERIALS USED IN THE BINDING MATRIX OR WALL MEMBRANE

The polymeric materials and other substances used as the binding matrix or membrane wall (encapsulation) in the various controlled release materials are listed in Table 4. This is not an all inclusive list in that the nature of the matrix or membrane substance cannot always be ascertained. However, this table does show the variety of polymeric categories used and certainly it indicates future trends. Polyamides, polyvinyls, and polyacrylates, for example, are used in encapsulating or binding insecticides and pheromones and these materials possess certain properties that render them useful obviously for such utilization.

The list of material sources or manufacturers (under Man. Code No.) is found at the end of Chapter V.

A toxicity rating is given using the categories in Clinical Toxicology of Commercial Products, Gleason, M. N. et.al. 3rd Edit., Williams & Wilkins Pub. Co., Baltimore, 1969. The code is shown below.

Toxicity Rating	Probable Lethal Dose (Human) (mg/kg)	Category
6	less than 5	Super Toxic
5	5 to 50	Extremely Toxic
4	50 to 500	Very Toxic
3	500 to 5 g/kg	Moderately Toxic
2	5 to 15 g/kg	Slightly Toxic
1	above 15 g/kg	Practically Non-toxic

TABLE 4
POLYMERS AND OTHER CARRIER MATERIALS

Material	Toxicity	Man. Code No.	EPA Ref. No.	Citation
Asphalt	-	-	62	372, 392
Beeswax	-	-	-	349
Camphene	-		-	276
Camphor	4		155	276
Carnauba Wax	-		-	342
Carboxymethylcellulose	1	16	-	299
Castor Wax	-		-	300
Cellulose acetate	-		-	244
Cellulose, anhydrous	-	16	-	277-389
Coal Tar	4	-	223	342
p-dichlorobenzene	3		632	276

Material	Toxicity	Man. Code No.	EPA Ref. No.	Citation
2,4-D: esters of				
poly (4-acryloxybutyl)	-	-	-	313
poly (2-acryloxyethyl)	-	-	-	313
poly (2-methacryloxyethyl)	-	-	-	313
2,4-D Starch Esters	-	-	-	340
Epoxy Compounds (General)	2 to 3	-	-	285
Gelatin	1	-	-	173, 200 230, 236 239
Hoechst Wax X-22	-	14	-	342
Lignin	-		-	332
Montan Wax®	-		-	273, 274
Menthol	4	-	540	276
Microcrystalline Wax	-	-	-	275
Naphthalene	3	-	587	276
Ozokerite (Hoechst Wax S)	-	14	-	342
Paraffin oil	1	-	-	286, 379
Paraffin Wax	1	-	-	297
Polyacrylic acid	-		-	174
Polyacrylics: Carboxylated	-		-	
Carboset 514	-	15	-	92, 101 370
Carboset 515	-	15	-	92, 101, 117
Carboset 525	-	15	-	92, 101, 117 118, 253, 280 369-370
Carboset 526	-	15	-	253, 280
Polyacrylonitrile	1		-	
Paracril (Hycar 1014)				
18% Acrylo	-	19	-	133, 352
22% Acrylo	-	15	-	133
26% Acrylo	-	15	-	133
Hycar 1043 34%	-	15	-	133
Hycar 1001 40%	-	15	-	133
52%	-	15	-	133
Polyalkylene oxide	-	-	-	289
Polyamide			-	186, 201, 230
Versamid 940	-	18	-	263
Plaskon 9407	-	20	-	293
Elvamide 8061	-	17	-	152, 293, 304
Elvamide 8062	-	17	-	152, 293, 304
Elvamide 8063	-	17	-	152, 293, 304
cis Polybutadiene	-	15	-	133

Material	Toxicity	Man. Code No.	EPA Ref. No.	Citation
Polychloroprene				
Neoprene WRT	-	17	-	27, 33, 131 352, 353
Neoprene GN	-	17	-	33
Neoprene AC	-	17	-	34
Polyethylene glycol	1 to 2	8	-	243
Polyethylene	1		675D	174, 281 390
Epolene E-10	-		-	286
Epolene E	-		-	287
Epolene N	-		-	287
Polyethylacrylate	-		-	296
Polyethylenimine	-		-	391
Polyethylene-Polypropylene	-		-	
Nordel 1070	-	17	-	129
Epcar 5465	-	15	-	324
Polyisobutylene	-		676A	
Vistanex LM-MS	-	21	-	
Polyisoprene				
Natural Rubber	-	-	-	35, 133, 310 362, 320 345, 352, 392
Polyisobutadiene				
Butyl LM-430	-	21	-	250
Butyl NBS 388	-		-	33
Polylactic Acid	-		-	339
Polynitrile				
Butakon A3003	-		-	34
Polypropylene	-	-	-	174, 281
Polystyrene-butadiene	-			296
Ameripol 1001	-	15	-	133
Ameripol 1013	-	15	-	133
Ameripol 1015	-	15	-	133
Polystyrene	-	-	-	281, 296
Polythiourea	-		-	341
Polyurethane	-	15		275
Isofoam PE-12	-	22		142, 152
Polyurea	-			203, 341
Polyvinyl Acetate	-			
Elvax Series	-	17		304
Polyvinyl alcohol	-	17	-	174, 296, 349
Sulfonated	-		-	349
Polyvinyl Chloride	-	15	-	262, 394, 396
Geon 135	-	15	-	153, 159, 304 305, 309, 310
Geon 121	-	15	-	153, 304, 309
Diamond 7502	-		-	255
Bakelite QYNV	-	8	-	275, 396

Material	Toxicity	Man. Code No.	EPA Ref. No.	Citation
Polyvinyl chloride/polyvinyl-acetate (VYHH)	-		-	40
Polyvinyl esters of 2,4-D	-	-	-	313, 344
Polyvinyl esters of Silvex	-	-	-	313
Polyvinylidene chloride			-	397
Polyvinylpyrrolidone	1		681	174
Rosin, wood	-	-	-	40
Rosin, pentaerythritol ester (Pentalyn 225)	-	3	-	342
Styrene-Maleic Anhydride Copolymer	-		-	42
Sulfur	3	-	812	374, 428
				382, 384
Terpene Resin	3			
Piccolite A	-		-	342
Piccolite A-115	-		-	342
Rosin, Short Oil (Trilac 25)	-		-	290
Trioxane	-		-	276
Urea-Formaldehyde Polymer	-	-	-	293, 346, 396
Vinyl-2,4,5-TCP-propionate polymer	-	-	-	344
Wood pitch	-	-	-	342
Wood resin	-	-	-	342

V. FORMULATION ADDITIVES

Various substances are used in the formulation of controlled release materials or products in order to vary the physical properties of the matrix/agent system. Such variation may be used to improve processing, increase physical strength, protect against environmental factors such as ultraviolet insolation, regulate rate of release, color, deodorization, detackification, plasticization, and so on. The tendency is to neglect these additives in assessing interactions of the formulated material with the environment. Table 5 lists such additives along with the manufacturer, appertaining references in this document, and the toxicological category where assessed. The list is not inclusive in that some additives are not reported in the available literature - or a generic title is provided that is of little use to our consideration. The list does not include water or other evaporable solvents used in the dispersion of the formulation. However, certain defoamers, emulsifying oil, etc. are listed in that their presence in the environment may be longer lasting than that of the control agent.

TABLE 5
ADDITIVES IN CONTROLLED RELEASE FORMULATIONS

Trade or Trivial Names		Chemical Names or Identification	Man Code No.	Toxicology Category	EPA No.	Ref.
1.	Alumina	Aluminum hydroxide	-	1	-	280
3.	Altax	Benzothiazyl disulfide	2		-	61
4.	-	Ammonium sulfate	-	-	48	70
5.	Advastab BC-9	(Antioxidant)	12	-	-	255
6.	Borax		-	3	108	277
7.	Butyl nicotinate				-	279
8.	Cellulose acetate	-	-	-	-	244
*9.	Coal tar	-	-	4	223	374
10.	Calcium carbonate	-	-	1	139	395
11.	Captax	2-mercaptobenzothiazole	2	3	541	89, 69
*12.	DOP	Dioctylphthalate di(2-ethylhexyl) phthalate	13	2 or 3	-	153, 281 305, 393 159, 255 310, 397
*13.	DMP	Dimethylphthalate	13	2 or 3	380	153, 281
*14.	DBP	Dibutylphthalate	13	2 or 3	292	153, 244 274
*15.	DIOP	Dioctylisophthalate	13	2	-	393
16.	DiCup 40C	Dicumyl peroxide	3		-	61
*17.	-	Diethyl phthalate	13	2 or 3	-	280, 281
18.	Diatomaceous Earth	-	-	-	-	299, 374
19.	-	Dimethyl sebacate		-	-	244
20.	EPC	Carbon black	5	-	-	
21	(NA-22)	Ethylene thiourea	17	-	-	133
22.	-	Epichlorhydrin		4	424	286
23.	Elvanol 50-42	Polyvinyl alcohol	17	-	-	
24.	FEF	Carbon black	5	-	-	133
25.	-	Glycerol	-	1	469	243

TABLE 5
ADDITIVES IN CONTROLLED RELEASE FORMULATIONS

	Trade or Trivial Names	Chemical Names or Identification	Man Code No.	Toxicology Category	EPA No.	Ref.
26.	Gypsum	Calcium sulfate	-	1	-	286
27.	HAF	Carbon black	5	-	-	133
28.	-	Hydroxyethyl cellulose	-	-	-	230
29.	Hi-sil	Silica		-	-	276
30.	-	Hexyl nicotinate		-	-	279
31.	ISAF	Carbon black	-	-	-	133
32.	-	Isobutylbenzoate		-	-	279
33.	-	Iron nitrate	-	3	-	338
34.	KAOLIN	Aluminum silicate	-	1	-	374
35.	-	Lauric acid	7	1	-	133
36.	-	Linoleic acid	-	1	-	332
37.	-	Magnesium oxide	-	3	-	133
38.	Microballoons BJO (BJO-0930)	(phenolic polymer)	8	-	-	64, 320
39.	MBTS	Mercaptobenzothiazole disulfide		3	-	133
40.	MICROCELL E	(cellulosic material)		-	-	299
41.	Mica	(silicates mixed)	-	-	-	346
42.	MARK C	(stabilizer)		-	-	45
43.	MARK WS	(stabilizer)		-	-	45
44.	NEOZONE D (PBNA)	Phenyl-B-napthylamine	17	-	-	33 133
45.	-	B-naphthol	-	4	590	286
46.	-	Oleic acid	-	1	619	133
47.	PERMALUX	(antioxidant)		-	-	
48.	-	Palmitic acid	-	-	-	133
49.	-	Potassium hydroxide	-	4	693	230
50.	Petrolatum		-	-	645A	297

TABLE 5
ADDITIVES IN CONTROLLED RELEASE FORMULATIONS

Trade or Trivial Names	Chemical Names or Identification	Man Code No.	Toxicology Category	EPA No.	Ref.
51. Petroleum Wax		-	-	-	61
52. -	Polyoxylene sorbitan monooleate		1	-	297
53. -	Stearic acid	-	-	-	133, 338
54. SANTOCURE CBTS	N-cyclohexyl 2-benzothiazylsulfenamide	11	-	-	133
55. -	Sulfur	-	3	812	61, 133 381
56. SRF	Carbon black	5	-	-	133
57. -	Sorbitan monooleate		1	-	297
58. NaPCP	Sodium pentachlorophenate	11	4	784	374
59. TMTD	Tetramethylthiuram disulfide	17		856	133
60. -	Trioctanoin		-	-	232
61. THIXIN E	Glycerol tris-12-hydroxystearate	26	-	-	252
62. TEA	Triethanolamine		2	886	297
63. Tallow Fatty Acid		-	1	-	297
64. UOP 688	N-phenyl-N'-2-octyl-phenylenediamine	25	-	-	225 230, 236
65. UCAR 680	(styrene-acrylic latex)	8	-	-	254
66. -	Zinc oxide	-	3		133
*67. -	Tricresyl phosphate	13	3	884	

*Materials also used as pesticides in other applications.

MANUFACTURER CODE

1. Westvaco Corp.
   North Charleston, S.C. 29406

2. R. T. Vanderbilt Co., Inc.
   230 Park Avenue
   New York, N.Y.

3. Hercules Company
   910 Market Street
   Wilmington, Delaware

4. Retzlof Chemical Co.
   Box 45296
   Houston, TX 77045

5. Cabot Corp.
   P.O. Box 1101
   Pampa, TX 70965

6. Kelco Corp.
   San Diego, CA

7. Eastman Kodak Co.
   343 State Street & Branches
   Rochester, NY 14650

8. Union Carbide Company
   Coating Material Division
   270 Park Avenue
   New York, NY 10017

9. Olin Corp.
   New Haven, Conn. 06504

10. Armak Company
    Box 1805
    Chicago, IL 60690

11. Monsanto
    800 N. Lindbergh Blvd.
    St. Louis, MO 63166

12. Carlisle Chemical Works
    New Brunswick, N.J. 08907

13. FMC Corp.
    Organic Chemicals Div.
    633 Third Avenue
    New York, NY 10017

MANUFACTURER CODE

14. Hoechst Akt.
6230 Frankfurt (M) 80
Postfach 800320
German Fed. Rep.

15. B. F. Goodrich Chemical Co.
6100 Oak Tree Blvd.
Cleveland, OH 44131

16. Hercules Company
910 Market Street
Wilmington, Delaware 19808

17. E. I. duPont
900 Wilson Road
Wilmington, Delaware 19803

18. General Mills Chemicals, Inc.
21360 Center Ridge Road
Cleveland, OH 44116

19. Uniroyal Chemical Co.
Bethany, Conn. 06525

20. Allied Chemical Corp.
Plastics Division
Morristown, N.J. 07960

21. Exxon Chemical Company
P.O. Box 3272
Houston, TX 77001

22. Witco Chemical Company
Isocyanate Products Division
P.O. Box 1681
Wilmington, Delaware 19899

23. Dow Chemical Co.
Midland, MI 48640

24. Universal Oil Products Company
State Highway 17
East Rutherford, N.J. 07073

25. Baker Castor Oil Co.
40 Ave. A
Bayonne, N.J. 07002

VI. CONTROLLED RELEASE PRODUCTS

Commercially available products pertinent to this investigation can be considered in two categories: (1) Formulations for field use wherein a toxic element is contained within a polymer, or enveloped by a polymer or other material, and (2) nontoxic dispensing systems which can retain and release with some measure of control a toxicant, repellent, pheromone, etc. The first category is comprised of the following products:

ALTOSID SR-10^{tm}	JHM
ALTOSID PS-10^{tm}	JHM
BIOMET SRM^{tm}	Molluscicide
CAP-CYC CBL-9B	Molluscicide growth regulator
ENVIROCAP C^{tm}	Algicide
HERCON ROACH TAPE^{tm} etc.	Insecticide - Also act on young as well as adults
INCRACIDE E-51^{tm}	Molluscicide and Herbicide
KILLMASTER^{tm}	Insecticide - Also act on young as well as adults
NOFOUL^{tm}	Antifoulant
NO-PEST Strip^{tm}	Insecticide
PENCAP M^{tm}	Insecticide
STAPH-CHECK^{tm}	Fungicide and Bactericide

Also in this category there are additional formulations with no known trade name as yet.

Polyethylene/Chlorpyrifos Blend 3714	Larvicide
Polyethylene/Fenac	Herbicide

In the second group known release systems include:

CONREL^{tm} (hollow fibers)
POROPLASTIC^{tm} (porous sheet plastic)
SUSTRELLE^{tm} (microbeads)
HERCON^{tm} Dispenser
MACROCAPSULE DISPENSER

In so far as possible a brief description of each is included in this chapter.

1. FORMULATED PRODUCTS

A. ALTOSID SR-10^{tm}

Altosid SR-10 is a controlled release product utilizing a Juvenile Hormone Mimic as the active agent and a polyamide as the carrier matrix. Methoprene; Isopropyl (E,E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate, also coded as ZR-515, is the active material.[140]

The formulation developed is based upon the occlusion of ALTOSID (ZR-515) in a polyamide. The release rate is governed by the solubility of the agent in the polymer and the partition coefficient between the Altosid/polymer and the environment; either air or water.

Altosid^{tm} (Zoecon Corp.) is nonpersistent, biodegradable and relatively nontoxic to nontarget species.[136] Degradation in sunlight is so rapid that this material would be practically and economically worthless in terms of the target species without incorporation in some CR matrix form. Safety to mammals, fish, shellfish, birds and non-target insects has been demonstrated.[402,403]

The SR-10 formulation is aimed at mosquito larvae where terminal morphogenetic effects are observed by treating 2nd, 3rd and 4th instar larvae.[404] Methoprene content is 10% by weight. Altosid has no effect on mosquito adults or pupae. This agent is a larval moulting hormone mimic affecting only the 4th instar 10 to 30 hours before pupation.[405]

The low persistency and relative environmental safety of methoprene has been demonstrated for the SR-10 formulation. Altosid PS-10 does not appear to have any deleterious effects on poultry nor do residues exceed 0.01 ppm in meat or 0.05 ppm in the eggs.[406] Altosid released in the lower gut and manure prevent emergence of adult house flies (*Musca domestica*) and lesser house flies (*Fannia spp*).

B. BioMet SRM^{tm}

BioMet SRM consists of a patented formulation of bis(tri-n-butyltin) oxide (TBTO*) in a natural rubber matrix. The resulting product is used as a molluscicide for snail control overseas. No registration petition has as yet been filed. All sales to date have been to Africa.

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*Trademark M&T CHEMICALS INC.

The active organotin compound slowly diffuses out of the natural rubber matrix into the treated water course. The nature of the agent(s) released is unknown. Release occurs for two or more years with biologically efficacious results in that the snail carriers of dread parasitic diseases are destroyed. Toxicological information concerning TBTO, a moderate poison, and some small amounts of environmental data are available.[19,26,67] Environmental chemical studies are underway with TBTO; however, no data concerning the nature or impact of the actual organotin released is available.

C. CAP-CYC

CAP-CYC is the trade name of 3M's encapsulated chlormequat, a plant growth regulator. Horticultural usefulness has been demonstrated.[387-389] The active agent, 2-chloroethyltrimethyl-ammonium chloride, is produced by the American Cyanamid Co.[407] The nature of the encapsulant and additives is unknown to the authors of this report. CAP-CYC is mentioned here and more information should be sought in that (1) the active ingredient is a herbicide and at high dosages it will destroy the plant while at recommended low dosages it slows growth in an advantageous manner and, (2) the encapsulated form appears to offer substantial advantages in horticultural use.

D. CBL-98

The experimental controlled release molluscicide CBL-98 was developed by the Creative Biology Laboratory (Barberton, Ohio) under the auspices of the World Health Organization.[63,66,408] Basically it is a natural rubber matrix containing tributyltin fluoride as the active ingredient. Laboratory tests and limited field evaluations in Rhodesia have been promising.[74,75,84,88,408,409] The release life is probably in excess of five years. Since use is contemplated only overseas (so far) no registration has been requested. The recipe is shown below:

A number of hundred pound lots of disc-shaped pellets have been produced to date. It is believed by the authors that this material will supplant the use of conventional molluscicides in many areas over the next decade.

TABLE 6
CBL-98 CONTROLLED RELEASE MOLLUSCICIDE 410

	Recipe Parts	%
Natural Rubber	100	67.71
HAF Carbon Black	10.2	6.77
Zinc Oxide	2.0	1.35
Stearic Acid	0.2	0.14
PBNA[1]	1.0	0.68
Sulfur	2.5	1.69
Altax[2]	2.0	1.35
TBTF[3]	30.0	21.31

1. Phenyl-B-naphthylamine
2. Benzothiazyl disulfide
3. Tributyltin fluoride

E. ENVIROCAP C

Envirocap-C, Experimental Permit No. 10556-EXP-2G, is a controlled release copper sulfate algicide using polyethylene and a wax in the enveloping matrix.[359] Technical literature is not available from the 3M Co.

F. ENVIROCAP D

Envirocap D is another experimental product consisting of Diquat aquatic herbicide in a controlled release matrix. As of this writing no further information is available.

G. FERTILIZERS

Although not of direct concern to the subject matter of this document it is noted that a number of controlled release fertilizing materials have been developed and several, such as those sold under the Osmocote trademark (Sierra Chemical Corp.) rely upon an enveloping sulfur and/or membrane to regulate release.

It is believed that the utilization of controlled release principles in the application of agricultural fertilizers will substantially reduce the total amount of agent used while enhancing crop production through greater utilization and a more even distribution of availability.

H. HERBICIDE 14ACE-B1

A 2,4-D (Butoxyethanol ester) containing natural rubber formulation was developed at the University of Akron under the auspices of the U.S. Army Corps of Engineers.[318] Laboratory and field efficacy have been demonstrated.[310,320,322] Due to the nature of vulcanized elastomers this material has been prepared as floating or sinking pellets and suspending strands permitting selective treatment of the phytozone of interest. 14ACE-B has been produced by the Creative Biology Laboratory (Barberton, Ohio) for Corps of Engineer's use. The registration status is unknown. Loss mechanism is through the diffusion-dissolution process and an over two year half-life predicted. The recipe is as follows:

TABLE 7
AQUATIC HERBICIDE 14ACE-B1

Ingredient	Recipe	
	Parts	%
Natural Rubber	100	64.94
Zinc Oxide	1.0	0.65
Stearic Acid	0.5	0.33
CBTS	2.0	1.30
TMTDS	1.0	0.65
Sulfur	0.5	0.33
Iron Oxide	20.0	12.99
2,4-D BEE	29.0	19.81

The present in-use material is modified from the original development by adding 20 parts iron oxide to adjust specific gravity and dropping the 2,4-D BEE from 30 parts to 29 parts. A floating version would eliminate the iron oxide additive. The so-called "suspender" is a six inch strand with a laminated "anchor" of 1/2 inch length at the distal end. The anchoring attachment is a modified version of the 14ACE-B1 recipe omitting iron oxide and adding 75 parts of zinc oxide.

I. HERCON ROACH TAPE

Hercon^{tm} roach tape is the first commercial product utilizing the Hercon dispenser. The product carries an EPA Reg. No. 8730-5. It is essentially a laminated strip construction containing Baygon, diazinon or chlorpyrifos as the active agent in a plastic reservoir. Baygon appears to be the preferred agent. Field studies against the German Cockroach, Blatella germanica, have been most successful and have demonstrated marked superiority over the use of conventional spray applications.[268,270] Fumigant action appears to be negligible, kill arising from target contact for several seconds.[270] The release system has been described.[411,412,436] A more complete description of the Hercon dispenser appears under B of Release Systems.

Environmental impact would seem to be minimal since the roach tape is fully recoverable.[413] A wide range of plastics can probably be used in constructing such systems, however, plastisol or melt type polyvinyl chlorides would appear to be preferred.

J. INCRACIDE E-51

Incracide^{tm} E-51 consists of a 50% active weight of copper sulfate monohydrate in an oil extended ethylene-propylene-terpolymer. Envisioned uses are as a molluscicide, algicide and selective herbicide. The material was developed by the Creative Biology Laboratory (Barberton, Ohio) under the sponsorship of the International Copper Research Organization (New York, N.Y.) Usage has been confined, to date, to overseas snail control and consequently no pesticide permit or registration has been requested.

The formulation is as follows:

TABLE 8
INCRACIDE E-51

Ingredient	Parts	%
Epcar 5465	100	31.81
HAF Carbon Black	50	15.91
Zinc Oxide	3.0	0.94
Captax	0.2	0.06
Sulfur	1.0	0.32
TMTD	1.0	0.32
Ammonium Sulfate	2.0	0.64
Copper Sulfate Monohydrate	157.2	50.00

A simple leach type loss mechanism is developed wherein copper sulfate monohydrate loss as the copper ion is controlled through (1) regulation of porosity via use of fine structured carbon black and the appropriate degree of crosslinking as developed through vulcanization (290°F at 30 minutes), and (2) regulation of surface pH through the concomitant release of ammonium ion preventing the buildup of a copper carbonate/copper hydroxide impermeable film barrier at the interface. A patent, based upon the simultaneous release of two materials, has been applied for (Walker, K.E. and Cardarelli, N.F. Serial 557,051; May 13, 1975).

K. KILLMASTER

Killmaster^{tm} is a paintable or sprayable 1% (Killmaster I) chlorpyrifos-containing formulation. It is applied by brush to critical areas harboring cockroaches, ants and silverfish in homes and business establishments. Killmaster I is EPA registered (26693-1).

Killmaster I

Cyclosol 52	96.90%
Chlorpyrifos	1.00%
Inert	2.10%

Killmaster I is produced by Positive Formulators, Inc. 1044 N. Jerrie Avenue, Tucson, Arisona 85711.

Efficacious release occurs as the agent blooms to the dry paint surface at a rate of 2.77% per week.[264,265,415]

L. NOFOUL^{tm}, Antifouling Rubber

B.F. Goodrich NOFOUL antifouling rubber is registered under number EST-1225-OH-1. EPA files regarding this product were not available to us during the search. B.F. Goodrich pioneered controlled release elastomeric formulations based upon the diffusion-dissolution release mechanism - such as the molluscicidal rubbers. An early controlled release elastomeric formulation employing the diffusion-dissolution release mechanism is provided below:

TABLE 9
ANTIFOULING ELASTOMER

Ingredient	Recipe Parts
Neoprene WRT	100.0
FEF Carbon Black	14.5
Magnesium Oxide	4.0
Zinc Oxide	5.0
Ethylene Thiourea (NA-22)	0.75
Mercaptobenzothiazyl Disulfide (MBTS)	1.0
Lauric Acid	3.0
Processing Oil	6.5
Phenyl-8-Napthylamine (PBNA)	2.0
Bis(tri-N-butyltim) Oxide (TBTO)	8.0

M. NO-PEST^{tm} STRIP

The Shell Chemical Co. NO PEST^{tm} Strip contains about 20% dichlorvos (DDVP, Vapona) in a stabilized polyvinyl chloride base. Examination of pertinent patents, such as Folkenner et.al.,[416] and analysis of purchased strip performed in the author's laboratory in 1969 indicate the following recipe:

Polyvinylchloride	40% to 80%
Plasticizer	0 to 40%
Stabilizers	0.2%
Vapona (93% DDVP)	20%

The PVC used to be Bakelite QYNV as mentioned in the patents, but work indicates that the likely material is Geon 101 EP (B.F. Goodrich Co.) using either dibutyl phthalate or dioctylphthalate as the plasticizer. Patent references to tricresylphosphate indicated its possible usage. On the basis of the varied U.S. and foreign patents examined, and our own analysis, it is likely that the Shell Company changes at will the PVC and plasticizer used.

No-Pest Strip was used in dairy and poultry operations in 1966 and appeared on the general market for home use in 1967. Vaporette^{tm} and Star-bar^{tm} (Thuron Industries) appear to be the same thing. Various protective collars for domestic pets are similarly polyvinyl chloride formulations containing from 5 to 10% dichlorvos.

Laboratory evaluation of the NO PEST Strip at the University of Akron indicated that the commercial product lost dichlorvos and the plasticizer in the vapor phase continuously with air exposure for 8 to 12 weeks. Rate of loss was temperature dependent. Air flow and humidity were not varied during this study - but would likely affect surface loss rate in the first instance and biological efficacy in the second.

Various solid and plastisol type polyvinyl chlorides were compounded with 20% dichlorvos. Analysis showed that without the presence of a plasticizer - the loss of the agent is infinitesimal. Thus it is assumed that the blooming phenomena wherein the excess plastisol migrates to the polymeric surface acts as a carrier for the agent. Dichlorvos is soluble to some extent in phthalate type plasticizers and completely insoluble in all PVC materials checked.

Plasticizer vapor loss from the commercial product represents about 30% of the total plasticizer available.

Dichlorvos loss is about 30 to 40% of the total amount present. Consequently the no-longer-functional strip contains considerable dichlorvos. In fact by slicing the strip to provide new surface the loss mechanism again comes into play - and the liberation of dichlorvos and plasticizer is reinstituted for perhaps 2 weeks.

Gillett et al. and others have concluded that the NO PEST Strip is "safe" as far as the release of the agent is concerned.[417] This issue, though, remains unresolved, and the dispute over safety to humans will likely continue.[418]

Investigators appear to have missed one vital point - humans breathing or otherwise absorbing dichlorvos, are also taking in any of a number of plasticizers of unknown health hazard.

N. PENNCAP-M

PENNCAP-M carries EPA registration numbers 4581-292 and 4581-324. The product is a formulation of methyl parathion encapsulated with a cross-linked nylon type polymer formed by the reaction of sebacoyl chloride and polymethylene polyphenylisocyanate with ethylene diamine and diethylenetriamine.[419,420]

The capsule wall carries an exemption under 40 CFR 180.1028. (433)(434) Radiotracer studies in the rat showed complete elimination of the wall material in the feces with no uptake in the intestinal wall, animal tissues, or excretion in the urine. Goat radiotracer studies showed no milk or tissue residues to 0.1 ppb (method sensitivity).[401] Crop uptake studies showed no crop uptake and leaching studies showed no release into leachate water (method sensitivity 0.1 ppb).[401] There were no adverse effects in rat and dog feeding studies at feeding levels up to 10,000 ppm (highest dose tested).[401] The capsulant did not move out of the soil and degradation to soluble nontoxic breakdown products gradually occurred.[401]

Encapsulation of the methylparathion dramatically reduces the oral and dermal toxicity thus decreasing the handling and environmental hazard normal to the conventional usage of methyl parathion.[421] Formation of highly toxic methyl paraxon that can take place with conventionally applied methyl parathion does not occur with the encapsulated material.[422]

O. STAPH-CHEK

STAPH-CHEK^{tm} is a bacteristatic fabric used in hospitals and other areas where pathogenic microbes are of concern. Specific products are mattress ticking and covers, pillow covers, blankets, linen bags, stretchers, cubicle curtains and the like. STPAH-CHEK, per se, is not a prime subject for this report - but it does represent a controlled release concept and the developments embodied in this material may well have other uses of environmental proportions. The invention is described in U.S. Patents 3,279,986; 3,705,938, and 3,857,934.[393,395] An organotin or other bactericide or bacteristat is incorporated in a polyvinyl chloride film laminated on a fabric base.

P. MISCELLANEOUS

Several other limited use controlled release products are available to the consumer market, and a controlled release chlorpyrifos material has been developed with a registration petition(s) just requested.

1. MEDICAPS

Medicaps are a systemic tree injection material that carries iron (to control chlorosis). This process appears to be much more efficacious than the conventional foliar sprays or soil treatment.[424,426] Materials such as ferric ammonium sulfate are incorporated in a polymeric capsule, providing slow release for up to 3 years.[426]

2. JOBES TREE SPIKES^{tm}

This product is composed of a fertilizer, with 16-8-8 or 12-6-6, and a rigid binder so that a unit can be driven via hammer into the root zone of a growing tree. Fertilizer loss over at least one growing season is cited.[427] Both efficacy and economy of labor and material are apparent.[427]

3. POLYETHYLENE/CHLORPYRIFOS BLEND M-3714

Efficacy has been discussed in Chapter 2 of this report. Environmentally the controlled release formulation appears to overcome certain deficiencies of conventional chlorpyrifos usage, such as algal blooms, reduction of predaceous insect populations and so on.[443]

In order to properly adjust the density of the finished formulation to produce a sinking granule, high density chlorinated polyethylene was used, or a blend of low density nonchlorinated with a chlorinated polyethylene.[429] EPA files were not available to use concerning this material and consequently the nature, trade name, etc., of the binding matrix is not know.

2. RELEASE SYSTEMS

A number of materials have recently been developed with a release mechanism that may be applicable for use with a variety of pest control agents. Besides devices aimed at controlled release, there are a large number of readily available substances from rubber bands to cigarette filter tips that have been tried with some degree of success. Again there are an even larger number of economical, readily available substances that have not been examined as dispenser, but that would predictably absorb, retain, and gradually release pest control agents. An instance of the latter is the foamed polyurethanes which hold and gradually release lubricating oils for 10 or more years.[430,431] The authors laboratory examination of such materials has demonstrated that they will retain various pheromones and insecticides with gradual release for at least several months.[431]

A. CONREL^{tm}

CONREL is the trade designation for a range of precision hollow fiber dispenser systems. Vapor pesticides or pheromones can be loaded in the fibers and through tailoring to specific diameters and length a controlled vapor release rate can be achieved. Advantages claimed are design flexibility, precision release control and generally efficient use of the agent. Disadvantages lie in lack of protection from air or light and in inability to vary rate at the field site. One likely limitation to usage arises from the vapor release characteristic. Toxicant loss in air and soil can probably be fairly well controlled; serious problems arise when the potential usage is in water. Efficacy has been demonstrated in the controlled release of pheromones for the elm bark beetle,[261] grape berry moth, [432] pink boll worm[433] and others.

The utility of the CONREL system is well demonstrated in the effective release of the three essential elm bark beetle pheromone components simultaneously at the proper ratios - each agent having a different vapor pressure.[433] The rate of release is a function of the number of fibers (in a bundle) and the fiber diameter.[398] Diffusion from the liquid-vapor interface within the fiber is rate controlling.

The fiber polymer can be an undrawn polyester (polyethylene terephthalate),[433] a polyamide, Delrin, Formaldehyde-ethylene oxide copolymer such as CEL-CON or other materials.

Efficacious lifetimes of 2 1/2 or more months have been noted, compared to perhaps several days with conventional pheromone usage.[432]

B. HERCON^tm DISPENSER

The Hercon^tm dispenser has been shown to be biologically efficacious as a release mechanism for insecticides and pheromones.[256,270] The Hercon dispenser, in its simplest form, is a 3-layer laminate with the inner layer containing the active ingredient. Thus, in "Roach Tape", a Hercon product now being marketed by Johnson Wax, the insecticide slowly diffuses out of the inner layer to the outer surface and continues to do so for at least one year under household conditions. Roaches contacting the 1" x 4" strips of the laminate, judiciously placed in households to effect control, are dispatched on contact.[434] Significant advantages of the Hercon product are safety in handling, virtually no hazard in use, and very little insecticide required to effect control.

The Hercon dispenser of insect sex attractants (pheromones) functions somewhat differently. The attractant, concentrated in the inner layer, diffuses out through the outer layers and evaporates from the outer surface without buildup of attractant. There are several advantages in this system,[239,240] which have resulted in this dispenser being the one most widely used by the USDA; e.g., it is used in the gypsy moth, pink bollworm, and boll weevil programs. Thus, the attractant--being in the inner layer--is protected from degradation by light, air, and weather. This can be important because very small amounts of degradation products have been shown to greatly diminish or cancel attraction of pheromones (e.g., the alcohols derived from the acetate pheromones inhibit attraction.[235]) Undoubtedly the effect was operating when Johnson and coworkers found the Hercon dispenser containing the boll weevil pheromone, a 4-component mixture of unstable compounds, remained effective for 12 weeks, and during this time it was 177% as effective as USDA's standard bait, which had to be changed weekly.[247] Several other formulations tested at the same time were less effective than the standard bait, including Conrel fibers. Another advantage is the fairly constant emission rate of pheromone, which can be set at optimum values (too high an emission rate can be repellent and too low a rate undetectable). The system is very flexible. To regulate emission, the outer laminate layers can be made thicker or thinner or a greater or lesser area of the dispenser (easily cut with a scissors) can be exposed. Optimum emission rates, which are different for each species, are thereby achieved. Also, the duration of effectiveness is readily regulated by increasing or decreasing the attractant content of the inner layer.

A wide range of plastics can be used with the dispenser, and apparently a rather broad spectrum of insect control agents are incorporable.[413] Nearly 100 different agents have been so incorporated.[436]

It has been stated that environmental impact of the Hercon pheromone dispensers in traps is minimized because they are fully recoverable.[413] The economics of recovery may be prohibitive under some circumstances. The possibility has also been proposed to use the Hercon sheets as a powder or granules and to distribute them by aircraft over forest lands in much the same way as the microcapsules were distributed to confuse insects seeking mates (like the gypsy moth). Although this material would not be recoverable, very little of it would be dispensed. For example, at 8 g disparlure/acre only 80-160 g/acre of the plastic would be dispensed. Environmental impact of so small an amount of material is likely to be nil.

C. MICROCAPSULE DISPENSER

A "Microcapsule Dispenser" produced by the Controlled Release Chemical Corp. of Sante Fe, New Mexico represents a method of dispensing pheromones and insecticides.[228]

D. POROPLASTIC^{tm} AND SUSTRELLE^{tm}

Poroplastic and Sustrelle are tradenames for gelled cellulose triacetate materials produced by Moleculon Research Corp. of Cambridge, Mass.[437] Cellulose triacetate is formed in an acidic nonhydrolyzable solvent and then contacted with a nonsolvent miscible with the processing solvent. The resulting gel has a high liquid content.

Sheets (poroplastic) and microbeads (sustrell) made from this process have an open-celled ultramicroporous structure. The liquid content is usually water and in order to add a control agent the water must be replaced by elution or perhaps other processes.[438] Fixation of the agent is through selective deliquification, evaporative precipitation, reaction precipitation, etc.

Payloads to 96% are feasible with release being diffusion controlled.[439]

At this time cost is far too high for practical usage. However, the system does function, sustained release is achieved and the rate of release controllable by control of porosity and concentration.[440]

E. NOTES

Controlled release of various agents through encapsulation has been discussed in various sections of this report. A full treatment of technique can be found in the Vandegaer text.[441]

VII. ENVIRONMENTAL IMPACT OF POLYMERS

Since many thousands of man-made polymers and certainly hundreds of natural polymers can be utilized in controlled release pesticide systems it would be a never-ending task to investigate (via literature search, etc.) the environmental impact of each one. In certain generic classifications, polyvinyl chloride for instance, there are hundreds of substances on the consumer market. The distinction within a generic group lies in differences in molecular weight, crosslink density, short and long chain branching, percentage of a specific atom (such as chlorine in the various PVC), monomer content, catalyst and other processing fragments arising from the polymerization system used. These variables apply only to the polymerized material prior to the use of additives such as stabilizers, fillers, plasticizers, etc.

In order to properly consider the fate of polymeric and other binding materials used, several categories were developed wherein the members have similar properties relative to environmental deterioration. Each category was considered separately, and a literature search conducted for pertinent information. It is recognized that variation of a critical parameter, such as average molecular weight, will make a significant difference in environmental interactions, but mostly in the rate of reaction rather than the type or mode of reaction. For example; a high molecular weight material will likely be more resistant to environmental influences than a low molecular weight version of the same substance. The latter will likely degrade at a faster rate. In both instances, the products of environmental reactions should be the same or similar.

It should be recognized that the polymeric material must degrade in some fashion before there can be any environmental impact in the chemical, biochemical or biological sense. With reference to soil or the beds of watercourses, it is conceivable, though barely, that the addition of a polymer to the ambient environment will result in physical changes. It is well known that the application of an inert material to soil aids in aeration. Thus, a nondegraded polymer plowed into soil will enhance soil aeration. Since the authors cannot visualize more than a few hundred pounds per acre of a given polymer being applied annually (a few pounds per acre being much more likely), and since the weight of an acre-foot of soil is in excess of a million pounds, the environmental impact after dilution would appear to be nil. If polymers for use in controlled release were completely inert - or their degradation rate was measured in geologic time - as occurs with glass, the cumulative aspect would be a matter of concern. However, all organic polymers degrade upon exposure to the outdoor environment, and with few exceptions their nature is completely obliterated after a number of decades.

Examination of the available scientific literature has disclosed two significant findings:

(1) A great deal is known and published concerning the effect of the environment on the organic polymer.

(2) Literally nothing is known about the effect of the organic polymer on the environment.

Accordingly, the effects of the environment on the polymeric materials are summarized, and speculation offered in lieu of hard facts on the impact of environmentally initiated breakdown products arising from such interactions.

Degradation arises from the following natural factors:

a. Insolation (especially ultraviolet)
b. Heat
c. Water erosion
d. Oxidation (oxygen and ozone attack)
e. Biological (bacteria, fungi, insect, etc.,) attack
f. Hydrolysis
g. Ionic attack (especially in salt and fresh water)

The general intent of those scientists and engineers working with polymers is to prevent environmental action detrimental to the properties of a commercial or consumer material or product. Consequently, the nature of environmental attack and degradation is measured (as it affects the polymer), and through compounding or engineering design, methods of circumventing such attack are developed. Thus, an abundance of literature relating to polymer degradation has arisen, but this literature has little to offer on the chemical nature of the breakdown products and residues arising from degradation, let alone the effects of such materials on the environment.

The following categories were selected for investigation:

a. Natural and synthetic natural rubber
b. Ethylene-propylene polymers
c. Cellulosic materials
d. Polyisobutylene
e. Styrene-butadiene copolymers
f. Polyacrylonitriles
g. Polyacrylates
h. Polyesters
i. Polyamides
j. Polyethylene
k. Polyvinyl chloride
l. Chloroprene polymers
m. Polyurethanes
n. Cis polybutadiene
o. Acetal copolymers

A. Natural and Synthetic Natural Rubber

Natural rubber is basically polyisoprene. However, the latex, as it is tapped from the *Hevea brasiliensis* tree contains many impurities such as fatty acids, sterols and a number of esters. The nonrubber hydrocarbon content literally varies from tree to tree. In this respect man-made natural rubber, synthetic polyisoprene, has greater uniformity of composition and impurities of a different nature, (e.g., unreacted monomer, catalytic fragments, etc.) than the natural product.

It is recognized that natural rubber degrades rapidly upon exposure to the environment. As the latex is taken from the tree, it is common to the art to add a preservative such as sodium sulfite to reduce bacterial attack. Such additives carry over to the processed rubber goods.

Other compounding of natural rubber is keyed to the improvement of resistance to several environmental parameters; u.v., visible and infrared radiation, especially as insolation; oxidation through O_2 or O_3 contact: and protection from microorganisms, bacteria in particular, although some forms of fungi also attack natural rubber. Thus, Micrococus, Pseudomonas, Mycobacterium, Streptomyces, and Nocardia have been implicated in the biodeterioration of natural rubber.[442] Also, various fungi, including Stemphylium, Aspergillus, Penicillium, Fusarium, and Actinomycetes, are known to severely degrade rubber.[443-445] Natural rubber goods, where exposed to soil, water (or high humidity) and direct insolation, are almost always compounded with fungicides and bactericides.[446-449]

Natural rubber latex, as taken from the tree, contains certain natural antioxidants. Since these protectants are destroyed during vulcanization, man-made substances are added during compounding to retard oxygen and ozone attack. Oxidation leads to degradation through chain scission. The nexus of attack is on the alpha hydrogens and at double bonds. Degradation products arising are various aldehydes, ketones, alcohols and ethers. Ozone attack is probably of minor importance save in the presence of ultraviolet radiation, usually of solar origin. O_3 reacts with double bonds, resulting in ozonide formation and chain scission. The rate of ozone attack is proportional to the degree of stress on the rubbery material. In practice various secondary amines, phenolics and phosphites are used to protect against oxygen and ozone induced degradation. In all instances ambient temperature profoundly affects degradation rates arising from attack through radiation, oxygen and ozone, and microorganisms.

The ultimate decomposition products of natural rubber, as they arise from oxidative attack and to a lesser degree from hydrolysis, are probably carbon dioxide, carbon, water and perhaps minor amounts of methane and ethane. Vulcanized rubber contains various sulfur-bearing materials used as curatives and accelerators. Therefore, it is likely that very small amounts of sulfur dioxide, hydrogen sulfide and possibly elemental sulfur would likewise be released. The ultimate degradation products are of little concern in regard to the environment. More immediate should be the question of the various products arising at each stage of decomposition: sulfonated aromatics, mercaptans, alcohols, ketones, aldehydes, etc. To the author's knowledge the intermediate products of decomposition of natural or synthetic natural rubber in the environment (soil and water) have never been properly identified.

Synthetic natural rubber, lacking proteinaceous materials and fatty acids, is less prone to microbial attack. However, bacteria and fungi do degrade synthetic polyisoprene, but at a slower rate (under similar conditions).[450]

Rubber formulations can be tailored to increase deterioration if this is desired. Increasing the fatty acid content accelerates bacterial and fungus attack. Peroxide-cured rubber, where the crosslinks are carbon to carbon, is more susceptible to attack than sulfur-cured materials where the crosslink is carbon-sulfur-carbon or carbon-sulfur-sulfur-carbon.[457]

Natural rubber-based materials contain various additives: vulcanizing agents, reinforcing fillers (carbon black, silicates), nonreinforcing fillers such as clays, accelerators, stabilizers, processing aids (especially oils and waxes), and antioxidants and microbicides (depending on service conditions). The rate of environmental deterioration and the breakdown products are predicated upon the amount and nature of the additives as well as of the polymer.[457] Consequently, it would be, in the final analysis, necessary to examine a given system and not just the polymer. The presence of free sulfur has led to Thiobacterium attack and sulfuric acid as a product.[452]

Chlorinated natural rubber is now in use in antifouling coatings and may see future use in other areas of controlled release technology. One example is the Parlon series (Hercules Inc., Wilmington, Delaware) of chlorinated materials containing 67% by weight of chlorine. The manufacturer claims excellent resistance to salt water and oxygen. In the author's experience these materials are highly resistant to biological attack of any sort, and they may be toxic to many microorganisms.

B. Ethylene-Propylene Polymers

Ethylene-propylene polymers appear to be far more resistant to microbial attack than polyisoprene.[442] These materials show relatively little degradation due to heat, humidity, or ultraviolet radiation judging from results observed under extreme tropical environment exposure conditions.[453] Sulfur-cured EP rubbers did show less resistance than peroxide-cured EP materials.

Inquiry made of the B.F. Goodrich Chemical Company concerning their ethylene-propylene materials disclosed that no quantitative information regarding environmental degradation is available.[454] Ethylene-propylene materials, in general, show excellent resistance to ozone and oxidation.[455] EP elastomers are also noted for resistance to heat degradation and hydrolysis.

C. Cellulosic Materials

Cellulosic materials in general degrade rapidly under environmental conditions by depolymerization as a result of weathering and microbial attack. Cellophane, for example, degrades rapidly when exposed to the atmosphere and insolation, but slowly when buried in soil.[456] Bacterial attack seems to be confined to chain ends as direct-chain scission did not occur in dry soil exposure. Bacterial decay is extremely rapid in loose moist soil, decomposition arising from random cleavage of the carbon backbone of the polymer.

Cellulose triacetate, used in the moleculon controlled release dispensers, appears to be nontoxic and nonirritating; it has been cleared for food contact usage.[457]

Cellulose and cellulose ethers having a low degree of substitution are susceptible to enzyme degradation arising from bacterial attack. If the degree of substitution is increased by adding alkoxyl or hydroxylalkoxyl groups for the hydrogen of the hydroxyls on the anhydroglucose ring, resistance to microbial attack increases. Such materials are hydrophilic and water soluble to varying degrees.

Cellulose gums (carboxymethylcellulose) are essentially nontoxic, nonsensitizing and nonirritating. They are used as gellants and thickeners in foods. Preservatives are used with these substances because they are attacked by bacteria and rapidly degraded.

D. Polyisobutylene and Butyl Rubber

Compounded butyl rubber materials are highly resistant to moisture, and fairly resistant to oxidative attack. These substances are generally stable but can be degraded through depolymerization by heat, oxygen (at elevated temperatures) and mechanical shear. Proper choice of additives, such as organic peroxides, will accelerate heat breakdown. Polyisobutylene materials, properly compounded, are nontoxic and approved for use in food packaging.

Since butyl rubber is a copolymer of isobutylene and isoprene, the ratio between the two will affect the physical characteristics of the product and their environmental resistance as well. Butyl rubber lends itself not only to sulfur cures, but also can be crosslinked with various peroxides and dioximes. The degree of environmental impact may be significantly different for the various materials prepared by curing the same base polymer with sulfur - as say opposed to lead peroxide.

Butyl rubber is attacked and ingested by termites.[458] Bacterial resistance is said to be good.[459] Chemical resistance is high. Consequently butyl rubber degradation upon exposure to natural environments can be expected to proceed very slowly. Chlorobutyl elastomers can be expected to have an even greater resistance to oxidation and microbiological attack.

The authors were unable to locate information regarding butyl, chlorobutyl, or polyisobutylene breakdown products that would form following exposure to soil or water.

E. Styrene-Butadiene Copolymers

As a rule styrene-butadiene polymers are very susceptible to attack by oxygen, ozone and ultraviolet radiation. Thus, the raw materials processor will add protectants such as 2,6-di-tert-butyl-4-methylphenol.[460] The butadiene segment of the copolymer tends to crosslink upon exposure to ionizing radiation and/or oxygen. The copolymers so attacked become brittle and the surface crazes and cracks; eventually, the polymer breaks into small chunks or powders. Such changes also occur where the polymer is subjected to the thermal changes or physical stress associated with weathering, water flow, etc.

Styrene-butadiene materials are emulsified during processing with a fatty acid and/or rosin acid, both of which can serve as attractants and foodstuffs to lower life forms. Whereas these polymers have considerably greater resistance to bacterial degradation, compared to natural rubber,[442] they are still seriously affected. Both bacteria and fungi seem to confine their attack to the nonhydrocarbon constituent of the rubber.[461] In tropical aging studies, SB appears to hold up well save for ozone-induced surface cracking.[453]

The breakdown products arising from bacterial attack or other biodeterioration of styrene-butadiene copolymers cannot be found in the literature surveyed.

F. Polyacrylonitriles

Polyacrylonitriles, which are copolymers of a butadiene and acrylonitrile, tend to be resistant to fungi and microbial breakdown. Unfortunately, field exposure has been made with acrylonitrile blends plus other materials, such as the highly resistant polyvinyl chlorides,[453] so that reliable data on the polymer itself are not available. These materials are also moderately resistant to thermal degradation, which increases as the acrylonitrile content increases. Water resistance is also high. Ozone rapidly degrades this group of polymers, and antiozonants are added in formulated materials.

G. Polyacrylates

Polyacrylate polymers are chemically saturated so that crosslinking cannot occur through sulfur or peroxide linkages between double bonds. This group of elastomers are cured with amines such as triethylenetetramine. Sulfur-containing chemicals are sometimes used as retardants. In amine cured formulations, microbial attack is rapid and dramatic; where sulfur chemicals such as benzothiazyl disulfide, a fungicide, are used, a degree of protection is afforded.

Carboxylated acrylic systems, such as the B.F. Goodrich Company Carboset^{tm} materials, are readily destroyed by microorganisms, especially fungi. However, observations in the laboratory and under tropical field conditions have demonstrated that the Carbosets are ingested by molluscs, various insects and probably nematodes. FDA regulations have adjudged such substances to be safe for use on human skin and in contact with foodstuffs. (FDA Reg. 121.2514, 121.2520, 121.2550, 121.2569, 121.2571). Carboset 514 has been declared acceptable under EPA para. 180.1001 (c), i.e., it has been exempted from the requirement of a tolerance when used in agriculture.[462] The following is quoted from reference:[462] "No data has been gathered by us, or to our knowledge others, on its (Carbosets) toxicity to fish or plants -- or any other segment of the biota. No ultimate fate or degradation tests in soil and water, persistency, or other environmental tests have been run by us." A B.F. Goodrich Company "expectation" that the polymers of polyacrylic acid, in soil, will only degrade through microbial action has been stated.[454]

H. Polyesters

Polyesters are thermosetting plastics long noted for their resistance to chemical and radiation-induced degradation. These materials are susceptible to chain scission through solvolytic reactions. Hydrolysis occurs, at least at elevated temperatures, resulting in some degree of depolymerization. Pyrolysis leads to the evolution of carbon dioxide and other volatile products. However, only 3 to 4% of the total decomposition product weight is gaseous.[463] Radiation (ultraviolet, etc.) should lead to gradual depolymerization by ester interchange. However, degradation through exposure to insolation will be dependent upon the type of polyester. Polymers with repeated $(CH_2CH_2)n$ units are the most stable; the introduction of carboxyl groups in the chain leads to decreased stability.

Breakdown products at elevated temperature include allyl alcohol, formaldehyde, acetaldehyde, CO_2 and CO_3, water, formic acid and acetic acid.[464]

Information regarding biodeterioration could not be located.

I. Polyamides

Polyamides degrade under the influence of heat and radiation into a wide range of materials. Decomposition products include simple hydrocarbons, cyclopentanone, carbon dioxide, carbon monoxide and water. Breakdown is probably through random chain scission. Under ambient radiation conditions, degradation of nylon materials in microcapsules is expected to be extremely slow.

Moisture plasticizes polyamide and serious degradation occurs when the climate is hot and dry. Very low relative humidity coupled with intense ultraviolet radiation leads to excessive deterioration of nylon-type polymers. Polyamide surfaces are susceptible to fungus growth, the available polypeptide linkages probably being attractive to microorganisms.[465] Attack appears to be confined to the surface and the biodegrading process, if indeed it occurs, would be slow.

Examination of manufacturer's literature indicates that environmental impact testing is not performed, and the scientific literature is also mute on this point. Exemptions from the requirement of establishing tolerances have been granted.[419,420]

J. Polyethylene "PE"

Polyethylene, chlorinated polyethylene and chlorosulfonated polyethylene (Hypalon^{tm}) have been used in controlled release matrices. The M-3714 material used by the Dow Chemical Co. in the Chlorpyrifos/PE controlled release larvicide may be a blend of chlorinated PE and the lower density nonchlorinated material. As a generality polyethylene is very resistant to environmental degradation and the chlorinated PE's even more so. It is reported that PE shows better resistance to deterioration than even the chloroprene rubber materials.[466]

PE materials are highly resistant to thermal degradation and temperatures in excess of 200°C in the presence of oxygen are necessary before noticeable chain scission occurs. Hypalon-type PE's likewise exhibit excellent thermal resistance to chemical degradation and are highly inert to ozone, oxygen and oxidizing materials due to its completely saturated chemical structure. Ultraviolet radiation induced degradation is observed for all three categories. U.V. radiation catalyzes oxidation, and in practice carbon blacks or other screening materials are used as protectants. Water absorption and hydrolysis are negligible. Thus, polyethylene used in underwater cable sheathing appears to have a very long functional life in sea water.

Hypalon compounds after 15 years in soil burial tests actually increased in tensile strength and modulus:[468] Eight years water immersion data showed no loss in tensile strength, but a drop in elongation, i.e., it became brittle. Both properties probably increase with increasing chlorine content and saturation.

Polyethylene materials are highly resistant to fungi and bacterial attack, as well as being nearly chemically inert.

K. Polyvinyl Chloride

Polyvinyl chloride materials appear to be inert towards deterioration by soil microorganisms. Degradation does occur, but it is dependent upon the plasticizer used. Polymers with phthalate and phosphate plasticizers are resistant whereas those with adipate, azelate and sebacate plasticizers are susceptible.[468] Attack is also influenced by the stabilizers used.

Vinyl polymers, unformulated or compounded with resistant plasticizers, are highly resistant to the marine chemical and biological environment. Vinyls are thermally stable up to at least 130°F. However, they are generally not weather resistant and suffer serious degrading effects from ultraviolet radiation.

Loss of plasticizer through volatility results in the discoloration, cracking and enbrittlement of the polymer. Although this phenomenon mitigates against many vinyl uses, the actual deterioration of the polymer per se may be minor.

Vinyls are resistant to degradation by himidity and salt spray. It is noted that various organotins are used as stabilizers in perhaps the majority of rigid PVC products. Organotins are likely to impart a biocidal property to the formulations greater than that arising from the chlorine content.

Thermal degradation of PVC at elevated temperatures leads to dehydrochlorination and thus HCl evolution.

L. Chloroprene Polymers

The presence of chlorine in the neoprene type materials renders them very resistant to fungi and bacteria attack.[465,469] Water resistance is moderate although subject to improvement through proper compounding. Oxidation rate in the natural environment is extremely low, and prolonged outdoor exposures of 30 or more years demonstrate very little degradation.[470] Neoprenes are thermally stable to 180°F, resistant to most chemical reactions and apparently quite resistant to ultraviolet radiation.

Neoprene is not ingestible by microorganisms, although various compounding additives may be. Moisture, bacteria and chemicals found in the soil do not appreciably affect neoprene.

M. Polyurethanes

Elastomers containing amide and amino groups are especially prone to fungi and bacterial attack. *Stemphylium*, *Aspergillus niger*, *Fusarium* and *Cephalosporium* attack and penetrate urethanes.[465] Polyester-based materials are subject to hydrolysis as well as microbial attack so that deterioration in soil or ground waters is probably rapid. Polyether-based urethanes are inherently resistant to water.

Polyurethanes are, however, quite resistant to chemical attack, and when appropriately formulated will provide excellent service; e.g., in sewage pipes where they are exposed to a harsh environment.

N. Cis Polybutadiene

Cis-1,4-polybutadiene is thermally stable to over 100°C. Environmental effects arising from prolonged exposure to soil, ground waters, etc. are not known. It is suspected that the deterioration processes observed with natural rubber would apply to polybutadiene rubber.

O. Acetal Copolymers

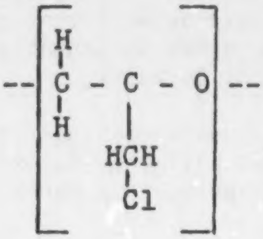
Acetal copolymers such as Delrin^{tm} (duPont) and Celcon^{tm} (Celanese Corp.) are used in controlled release dispensers such as the CONREL^{tm} system. Cel-Con is a formaldehyde-ethylene oxide material. Of interest is the fact that this group of copolymers should degrade in soil or water to formaldehyde and ethylene oxide, both registered as fumigants. Decomposition is rapid under ultraviolet irradiation, and in the presence of moisture, slow hydrolysis proceeds. Thermal degradation under temperatures of a natural environment would be extremely slow.[471]

P. Other Materials

Silicon rubber has not, to our knowledge, been utilized in controlled release pesticide systems. However, present usage in CR drug dispensing systems makes it a likely candidate for future CR pesticide applications. Silicones are heat and moisture stable. Most silicones are recognized as nontoxic and extremely inert to biological attack. Under environmental conditions their deterioration would be very slow.

Polyacrylamides should also lend themselves to CR usage. These materials degrade slowly under the influence of heat. In the presence of moisture, it is anticipated that polyacrylamides will gradually depolymerize and liberate ammonia (alkaline conditions) or ammonium salts (acidic conditions).

Another possibility for use in CR formulations is Hydrin rubber:



$$-\!- \left[\overset{\text{H}}{\underset{\text{H}}{\text{C}}} - \underset{\underset{\text{Cl}}{\text{HCH}}}{\text{C}} - \text{O} \right] -\!-$$

the homopolymer of epichlorhydrin. This material shows extreme stability to heat and ozone. Cure systems used depend upon diamines for cross-linking, which would indicate that Hydrin rubber is susceptible to microbiological attack.

Silica-modified polyvinylchlorides or vinyl chloride-vinyl acetate copolymers, commercially marketed as Microporous Plastic Sheet (Amerace Corp.), would appear to be likely candidates for dispensing pheromones and various volatile fumigants.[472,473]

* * *

Manufacturer's literature such as specification sheets, brochures, reports, etc. were examined for all polymers listed in Chapter IV. No reference was found to the products arising from radiative, oxidative, or biological degradation of the polymers.

Without developing a treatise on polymeric chemistry it may be useful at this point to note the types of polymeric reactions possible under foreseeable environmental conditions.

1. Cleavage reactions

    a) Hydrolysis
    b) Oxidation
    c) Ozonization
    d) Ultraviolet radiation
    e) Thermal rupture of bonds

2. Surface reactions

    a) Grafting (through incident U.V. radiation)
    b) Chemical reactions with reactive environmental materials, especially ionic constituents of ground water.

3. Intermolecular reactions

    a) Crosslinking by U.V. (or visible light!)
    b) Crosslinking through the presence of free monomers.
    c) Crosslinking through the presence of active ions in soil or water.

VIII. ENVIRONMENTAL IMPACT OF ADDITIVES

What little data are available pertinent to the impact of formulated polymers in the natural air, water and soil environment indicates that the nonhalogenated materials decompose into nontoxic substituents. However, formulated polymers amenable to use in controlled release systems contain additives that improve physical properties, assist in processing, or offer protection from environmental damage by insolation, oxygen, moisture, etc. The degradation of a given formulation will, therefore, release chemicals other than the active ingredient per se or residues of the polymer.

The additives in CR formulations are listed in Chapter V. Literature on each substance was examined for environmental impact. Table 10 again lists these materials and describes their environmental impact in accordance with the following classification key:

1. A natural product with no detrimental impact expected.

2. A chemical that is essentially nontoxic and should remain unchanged in the environment.

3. Materials ingestible by microorganisms, which act as nutrients, or plant nutrients, or trace materials vital to plant (or animal) nutrition.

4. Materials of low toxicity that may degrade to simpler chemicals of higher toxicity.

5. Materials of low to moderate toxicity to plants and/or animals.

6. Toxic substances that will affect exposed plants or animals, but will degrade to nontoxic chemicals in time.

7. Unknown.

8. Material that will degrade to highly toxic substances.

9. Essentially nontoxic material that should degrade to a nontoxic material.

The classification is solely that of the author (NFC) and must be accepted as no more than an enlightened opinion. The type of environmental impact data desired is not available in the literature examined.

TABLE 10

ENVIRONMENTAL - IMPACT ASSESSMENT OF ADDITIVES

Material	Class
Aluminum hydroxide	2
Advastab BC-9	7
Borax	1
Butyl nicotinate	3
Cellulose acetate	3
Coal tar	1
Dioctylphthalate	5
Dimethylphthalate	6
Dibutylphthalate	6
Dioctylisophthalate	6
Dicumyl peroxide	7
Diethyl phthalate	6
Diatomaceous earth	1
Dimethyl sebacate	
Carbon black	3
Ethylene thiourea	6
Epichlorhydrin	4
Polyvinyl alcohol	9
Glycerol	3,9
Gypsum	1
Hydroxyethyl cellulose	3
Hisil	1
Hexyl nicotinate	3
Isobutyl benzoate	3
Iron nitrate	9
Kaolin	1
Lauric acid	1,3
Linoleic acid	1,3
Magnesium oxide	2
Microballoons (phenolic)	2
Mercaptobenzothiazole	4
Mercaptobenzothiazole disulfide	4
Microcell E	1
Mica	1

Material	Class
Phenyl-B-napthylamine	3(?), 4, 6(?)
B-naphthol	6
Oleic acid	1,3
Permalux	7
Palmitic acid	1,3
Potassium hydroxide	9 (depends on amount)
Petrolatum	1,3
Polyoxylene sorbitan monooleate	3
Stearic acid	3
N-cyclohexyl-2-benzothiazyl-sulfenamide	4
Sulfur	1,3
Sorbitan monooleate	3
Tetramethylthiuram disulfide	4
Trioctanoin	1,3
Glycerol tris 12-hydroxystearate	3
Triethanolamine	3
Tallow	1,3
N-phenyl-N-2-octyl-phenylenediamine	3(?)
UCAR 680	7
Zinc oxide	1

IX. TEST PROCEDURES

Tests commonly performed on polymeric materials are keyed to the determination of resistance to environmental forces. Most evaluatory methods deal with physical properties such as tensile strength, stress-strain properties and so forth. Methods pertinent to the subject area are relatively few and are aimed at evaluating the effects of the environment on performance characteristics of the polymer and not on the environmental impact. Standard test methods are found in the ASTM volumes, various military specifications and often within industrial files. A search of current ASTM literature disclosed no test methodology that directly measures environmental impact. However, a number of tests are useful in that they could be modified in such a manner as to provide data pertinent to the impact question. Such ASTM methods and standard practices are listed below:

D570-63 (1972)	Water absorption of plastics
D573-67(1972)	Accelerated aging of vulcanized rubber by the Oven Method.
D471-75	Change in properties of elastomeric vulcanizates resulting from immersion in liquids.
D750-68 (1974)	Operating light and weather-exposure apparatus (carbon-arc type) for artificial weather testing of rubber compounds.
D746-73	Brittleness temperature of plastics and elastomers by impact.
D1149-64 (1970)	Accelerated ozone cracking of vulcanized rubber.
D1171-68 (1974)	Weather resistance exposure of automotive rubber compounds.
D1278-72	Chemical analysis of natural rubber.
D1416-74	Chemical analysis of synthetic elastomers.
D1435-69	Outdoor weathering of plastics.
D1499-64 (1971)	Operating light and water exposure apparatus (carbon-arc type) for exposure of plastics.
D1501-71	Exposure of plastics to fluorescent sunlamp.
D1693-70	Environmental stress-cracking of ethylene plastics.
D2445-69	Thermal oxidative stability of propylene plastics.
D2565-70	Operating xenon arc-type (water-cooled) light- and water-exposure apparatus for exposure of plastics.
D3045-74	Heat aging of plastics without load.
E171-63 (1972)	Standard atmospheres for conditioning and testing material. (As based on D618)
G21-70	Determining resistance of synthetic polymeric materials to fungi.

G22-67T	Determining resistance of plastics to bacteria.
G23-69	Operating light- and water-exposure apparatus (carbon-arc type) for exposure of nonmetallic materials.

A very large body of military specifications were not available for search. Procedures, such as MIL-F-13927-A regarding Mold, Mildew and Fungus Resistance are pertinent.

It is important to note that the available standard test methods regarding microbial degradation do not draw a clear distinction between surface growth and surface attack and actual penetration of the polymer by bacteria and/or fungi.

Soil burial test procedures are numerous, but all emphasize effect on the polymer. The Booth and Robb report describing soil preparation, incubation method, etc. is useful.[468] Unfortunately, different soils are supportive to different microbial populations (and numbers), moisture contents, ion contents and so on. Thus, correlating results from various laboratories into a composite picture is difficult.

The diffusion of water into a polymeric formulation is an important consideration not only in hydrolysis but also in bacterial attack where moisture is essential. Also matrix porosity allows the entry of ion-rich water thus speeding degradation through chemical decoupling of the polymer backbone and/or side chain scission.

Many of the tests performed in order to determine the fate of pesticides in the environment are probably adaptable to the evaluation of polymer residues, breakdown products, and metabolites. Furmidge, et. al. describe a laboratory leaching apparatus that could be of value in this respect.[13] As these authors mention, the breakdown of inert pesticide carriers is often dependent on water movement into the granule. Methods used in detecting, measuring and monitoring diffusion of pesticides in soil should be adaptable to the similar detection and monitoring of polymer breakdown product movement.[329] A moist sand test for Aldicarb could be used as well for the breakdown products of the encapsulating polymer, perhaps determining both agent and polymer fates simultaneously.[293] Likewise, methods used in measuring pheromone emission rates might be adaptable to the detection and analysis of polymeric gaseous breakdown products.[474]

It can be generally concluded from reviewing the literature that current standardized test procedures will not provide the information necessary for the determination of environmental impact.

X. TEST CRITERIA

The basic purpose in establishing a method of determining environmental impact is to ascertain the effects of a polymer formulation on all aspects of the environment. It is the authors' contention that present methods of evaluating pesticides and other nonpolymeric materials are only of partial value towards assessing environmental impact. For instance, many areas where polymeric formulations could interact detrimentally within the use environment are not covered and various laboratory type tests used in establishing toxicity and other factors are not translatable to an environmental situation. An environment represents a complex interaction of physical, chemical and biological forces. In the usual laboratory test only one parameter is usually varied. It is believed that any assessment of environmental impact must, in the final analysis, be based upon an environmental test situation.

A number of pertinent points ought to be considered at this juncture:

(1) It may not be possible to consider only the polymer. Polymer and agent (active ingredient) may interact in affecting the environment, just as two agents can provide synergistic effects.[475]

(2) Additives used in polymer based formulations may synergize environmental impact as well as accelerate the rate of biodeterioration.[465,468]

(3) Polymeric formulations can be tailored to retard or enhance deterioration through the use of additives, variation in cross-link density, addition of hydrolyzable groups to the polymer backbone, type of additive used in terminating chains and so forth.[298]

(4) Environmental influences can block degradation through chemical combination, as is observed with various pesticidal agents.[302,476]

(5) In many control situations two or more agents will be incorporated in the same pellet (granule, etc.) or two or more agents in two or more polymers added to the same pest infested environment. For example, to prevent bacteria and algae in potable water, and swimming pools, both a bactericide and algicide would be used simultaneously.[477]

In a comprehensive evaluation program keyed to the determination of the environmental impact of a polymer-additives-agent system, the initial step would lie in the performance of those laboratory procedures now in use to determine toxicological properties. Tests performed with the agent alone ought also to be undertaken with the agent-additives-polymer combination and the polymer-additives base alone.

The thrust of this report is to deal with polymer and polymer additives alone; so agent systems will not be discussed.

Polymeric materials, as formulations lacking only the active agent, ought to be subjected to various toxicological tests in order to assess the nature, if any, of a potential hazard involved. This is generally required by regulations; however, various polymeric materials have been granted exemptions based apparently on data unknown to the authors. For adequate toxicological characterization, it is believed that the following tests ought to be performed as appropriate to the end use:

Acute oral toxicity (2 to 5 days)
Subacute oral toxicity (90 days)
Primary eye irritation
Primary dermal irritation
Acute dermal toxicity
Subacute dermal toxicity
Acute inhalation toxicity
Teratology
Lethal mutagenicity (acute and chronic)

Such studies would include representative organisms of the use environment: mammals, fish, fowl, insects, vascular plants, plankton, etc. For proper characterization, not only the formulated material (sans agent), but also the breakdown products of that material should be examined. A polymer (and its additives) exposed to the environment may (or may not) break down into residues of varying lifetimes, of varying toxicity to life forms, at varying rates, depending on the nature of that environment. The best method of determining the breakdown rates, nature of residues, etc., is to conduct biological and chemical evaluations in the use environment. However, one material may be used in a multiplicity of environments, and the chemodynamics of a given system may vary significantly from environment to environment. A generalized classification may not be prudent; i.e., one cannot claim that a controlled release material made for use in soil ought not to be examined for aquatic effects.

After the laboratory toxicity tests are performed on the polymer-additive system, the next logical step would be to determine the mode of polymer and additive breakdown from the chemical and physical standpoint. It is realized, or course, that as the polymer degrades, additives will be released in chemically intact form or perhaps themselves broken into various degradation products. The picture can be complex.

In examining the Guidelines for Registering Pesticides in the United States a number of rules regarding tests are provided for use in assessing polymer decomposition. They are as listed:[478]

Hydrolysis rate 162.78 (b)(4)(ix)
Stability 162.78 (b)(4)(xii)
Oxidizing/reducing agent capability 162.78 (d)(5)
Basic soil metabolism (162.8)(b)(3)(ii) & 162.79 (a)(2)(v)
Abbreviated soil metabolism 162.8 (b)(3)(ii) & 162.79(a)(2)(vi)
Soil metabolism, bound residue studies 162.8 (b)(3)(ii) & 162.79 (a)(2)(vii)
Soil metabolism, anaerobic 162.8 (b)(3)(ii) & 162.79 (a)(2)(ix)
Soil persistence 162.8(b)(3)(ii) & 162.79(a)(3)(i)
Soil persistence, long term studies 162.8(b)(3)(ii) & 162.79 (a)(3)(v)
Leaching studies-field 162.8(b)(3)(ii) & 162.79(a)(4)
Degradation in water containing suspended solids 162.8(b)(3)(ii) & 162.79(b)(2)
Degradation in bottom sediments 162.8(b)(3)(ii) & 162.79(b)(3)
Translocation: Uptake from aquatic sources 162.8(b)(3)(ii) & 162.79(b)(4)(i)
Moving water tests 162.8(b)(3)(ii) & 162.79(b)(6)
Crop uptake: Soil 162.79(c)(2)
Photodegradation 162.79(d), 162.8(b)(3)(ii) 162.79(b)(1)(ii)(d) & 162.79(d)
Effect on microorganisms 162.8(b)(3)(ii) & 162.79 (f)(2)

These tests can, of course, be tailored to determine polymer interactions. However, the critical work that should be performed is to determine residue effects. In the same manner that the fate of a pesticide is examined in the environment (see EPA 660/3-74-025 for example), the polymer/additives combination should be similarly determined.[479,450]

It is not the purpose of this report to develop test methods keyed to an elucidation of the degradation of polymers (and additives) under environmental influences. That would represent a major undertaking, of necessity buttressed by considerable laboratory work. It is pointed out that the knowledge is readily available for such developments.

Tests ought to be developed based upon the nature of plant and animal response to materials foreign to their environment. Works such as that by Levitt and Treshow will establish the empirical base.[481,482] Tests common to the determination of pesticide fate in plants and animals can be conducted using polymers and polymer-additives systems. For instance methods of assay procedures for pesticide residues,[483] determination of metabolic pathways and fate of the material within a living organism [484-486] could certainly be modified for use in the subject area.

Tests commonly utilized in the evaluation of polymer resistance to environmental factors could likewise be varied to permit the analysis of degradation residues and metabolites.

It is believed that the so called "weatherometer" type tests such as specified in ASTM recommended practices and procedures G23-69, E171-63, D2565-70, D1499-64, D1171-68, D750-68, and D1435-69 could be used to expose polymeric materials and formulations to a simulated natural environment under accelerated degradation rates. The breakdown products that result could be isolated from the test chambers and analyzed by conventional techniques. Obviously, in the development of such procedures a preliminary correlation study comparing degradation in an outdoor natural setting to the laboratory method would be essential to the determination of the accelerative factor.

It is believed that the water absorption procedures and accelerated hydrolysis type tests as described in ASTM D570-63, and D471-75 can also be used as exposure criteria followed by an analysis of the breakdown materials.

Supportive procedures such as oven aging and heat lamp exposure tests (ASTM D3045-74, D2445-69, D1693-70, D1501-71 and D573-67) would also provide valuable information regarding the nature of polymer degradation. In each instance it is only a matter of sampling for residues at varying exposure periods and analysis. Low temperature effects can be similarly determined through any of a number of standard procedures, e.g. ASTM D746-73. The stresses of depressed temperature environments lead to chain scission, loss of additives and other noteworthy effects. Accelerated tests involving oxidation and ozonation are also valuable as a guide to environmental behavior.

Analysis of the chemical milieu arising from degradation tests can be performed by common chemical methods. Both the degradation products which will literally "fall off" or be washed off with or without solvation must be examined as to their chemical nature and toxicological potential. Likewise the apparently intact controlled release pellet, granule, dispensing system, etc. would also be examined for changes in its nature due to the loss of volatile components, additives, chain ends and so on. Perhaps the basic ASTM D1278-72 and D1464-74 analytical procedures could be utilized.

There is considerable extant literature regarding the general mode of polymer degradation under exposure to insolation, elevated temperatures, ozone, oxygen, rain fall, and salt spray. The literature describes, as a rule, the physical changes in the degraded material, e.g. loss of molecular weight, and not the chemical nature of the degradants. However, tests performed in such studies may be modified to suit the needs of environmental impact studies.

The standard practices used in evaluating fungi and bacterial resistance in various laboratory environments, including soil burial tests, could also serve as the initiation point for developing methods of measuring the chemical nature of biodeterioration and the structure and toxicology of the resulting metabolites. ASTM G21-70 and G22-67T might be appropriate starting points.

Analysis of polymer and polymer additives in soil represent somewhat unique problems although again a large body of literature is available describing environmental analysis. The works by Ahuja et al. will serve as an example.[487] The problems associated with the detection of minute pesticide residues will also be faced when examining a natural situation for polymer/additive residues.[488]

XI. CONCLUSIONS AND CRITIQUE

A. Controlled Release Pesticides; an Emerging Technology

Agricultural and public health pest control techniques rest upon large-scale usage of toxic materials that usually destroy hostile life forms through acute intoxication. These materials are sometimes persistent, highly toxic to the target species and often to nontarget life, may contaminate soil, water and the atmosphere, and may impair the health of humans. Ecological impact from such usage -- if unregulated -- can, in time, bring about an environmental situation detrimental to the well-being of humanity.

An obvious approach is to minimize the use of pesticides by substituting less disruptive methods of controlling pest life. Biological control is thought by some to offer a viable alternative. Such control may be through the use of natural predators or competitors that reduce the pest population without untoward effects on nontarget biota. Although this approach is an appealing one, most experts agree that today's need of food and fiber cannot be met by this approach, and its reality appears to be limited in scope. Furthermore, the introduction of new life forms, usually from other distant habitats, is fraught with danger, and very exacting evaluations of the environmental impact of the introduced insect, pathogen, or parasite must be made. Such studies require years, even decades, and thus offer little immediate hope that this nation can increase food output and carry out important public health measures while decreasing environmental contamination. Also it is likely that some major pests do not have acceptable biological controls.

Another biological approach lies in the release of chemical agents that are not toxic per se to the pest, but intervene destructively in some aspect of the life cycle so that the population is reduced. Insect growth regulators and sex attractants used as confusants are two types of materials under investigation. In both instances it is noted that a chemical agent is released in the environment (and may well have an effect on nontarget life), and efficacy will almost certainly demand that the agent be released over some extended duration, several months (gypsy moth) to a year or more (fruit fly). The release mechanism involved will almost certainly be based upon the incorporation or encapsulation of the agent in a polymeric substance and the controlled dispersal of that substance in the environment.

Combination approaches utilizing a nontoxic pheromone and a toxic agent are under evaluation. Fruit fly baits wherein a sex attractant is combined with an organophosphorus toxicant in a "bait" is one example. It is likely that much less pesticide will be used to effect control in this case; however, attractant, toxicant and the binding matrix will be dispersed in the environment and thus have some degree of impact. In any case, only relatively few pests can be controlled economically and satisfactorily in this manner based upon present day knowledge.

Land management and cultural practices can be greatly improved with a commensurate drop in agricultural pesticide usage. However, this approach is limited in scope and literally requires that the farmer possess expertise in biology, ecology, climatology and other sciences, an unlikely supposition.

The alternatives mentioned above are viable to some extent but they are not practical or available now, or in many instances they are years away. Chemical pesticides will predictably be in use for many years, although perhaps being gradually decreased as more environmentally safe methods are introduced.

One potential, but immediate answer to resolving the antagonism between increasing crop output and protecting health while still reducing environmental hazard or impact lies in improving present pesticide formulations and/or dispersal methods so that substantially less chemical is used, or environmentally safer materials, such as nonpersistent pesticides, replace existing substances. Controlled release pesticide formulations which act through an acute or a chronic-intoxication mechanism and utilize nonpersistent agents must be considered as a logical alternative to conventional large-scale dosing techniques.

Controlled release materials have been shown in laboratory and field evaluations to provide pest control at ultralow concentrations of non-persistent toxicants. In several instances, such materials have reached the commercial market and are efficacious though using only 10% or less toxicant than that normal to conventional control. The rate of invention and introduction of controlled release technology can match the increasing demands of the farmer for pest control materials, provided that there is incentive for the pest chemicals industry to move in this direction. The use of smaller amounts of chemicals does not, in itself, entice manufacturers to examine controlled release. As raw materials cost increases with decreasing petroleum supply, this approach may become more attractive. Perhaps the best motivation for a hard look by industry at this area will be the show of interest by the Environmental Protection Agency in expanded use of CR products that utilize less-than-conventional amounts of pesticides and do so with less hazard.

Interest in the use of controlled release pesticide systems based on polymeric matrices or membranes is accelerating. Whereas five years ago only a handful of technologists were involved, the authors now note that dozens of companies and governmental groups are working in the area or planning an entry.

Controlled release materials possess a number of inherent advantages over conventional formulations. In general they are safer for human handling in that the pellet surface, at any given time, contains only an extremely small quantity of toxicant. If one spills an emulsion or solution of pesticide on the skin, the consequences can be grim. Dermal penetration of organophosphorus materials, for instance, can be rapid and fatal. A "spill" of controlled-release pellets would seem to be rather innocuous. Ingestion of conventional pesticide emulsions or granules or the inhalation of wettable powders or dust would constitute considerable hazard. One cannot conveniently inhale enough of a toxicant from a controlled release pellet to constitute a hazard. Likewise, children or nontarget animals that might ingest a CR pellet are not apt to be harmed. Elastomers, so far as is known, are not digestible, and in the few evaluations performed, they pass through the gut and are excreted reasonably unaffected. Loss of toxicant during pellet passage through the gastrointestinal tract should be very low. The recent advent and testing of encapsulated methyl parathion supports this thesis, oral LD values being drastically increased over that of the nonencapsulated material.

Controlled release pesticides formulated in solid elastomers or plastics can be fabricated in any number of shapes and sizes consistent with rubber industry technology. Sheet, strands, strips, granules, pellets, tubes, any shape that polymers can normally be molded. Thus, a given substance can be conveniently tailored to best suit the use environment. The armamentarium of controlled release elastomer-based pesticides is far greater than the few forms in which conventional pesticides are processed.

Encapsulated formulations and dispensing systems can likewise be manufactured in designs that provide optimal efficacy, and as a result the use rate of the given agent can be reduced.

It cannot be reasonably disputed that continuous exposure of the target pest to ultralow pesticide concentrations leads to a condition of chronic intoxication terminating in mortality. Both snails and aquatic weeds exhibit chronic symptoms and not the acute effects seen with high-level dosing. Even the mode of mortality differs. Evidence exists that the so-called "chronicity" phenomenon is also observed in insecticide studies and experiments with growth regulators.

Our present hypothesis is that the chemoreceptors of snails fail to sense the presence of ultralow molluscicide concentrations and thus the target does not react through avoidance mechanisms or physiological defense. In the case of aquatic weeds we believe that the very low dosages fail to trigger the inherent defense mechanisms common to plants so that translocation of the herbicide to the site of lethal action is unhampered. This contention is being experimentally examined now and all evidence to date is positive for the systems studied.

Acute intoxication, by its nature, requires relatively large dosages of chemical control agents to overcome target defense.

The advantages of controlled release are numerous and well documented in current literature.[489-491] The authors likewise agree that the controlled release method of dispersing pesticides will have a much lower degree of undesirable environmental effects compared to effects with conventional techniques that perforce rely on the application of large quantities of hazardous chemicals to the environment.

Of course controlled release toxicant systems can be utilized in such a manner as to reduce the target population through acute intoxication and, indeed, most commercial and experimental systems function in that manner. However, release is not long term compared to that seen with the elastomer/herbicide or elastomer/molluscicide systems reported herein.

2. Disadvantages of CR Systems

Controlled pesticide delivery systems are of such recent vintage that relatively little is known concerning disadvantages. One vital area lies in assessment of the development of resistance or tolerance triggered by long term sublethal exposures within a given pest population. However, our charge is to examine the implications of burdening the environment with varying amounts of the carrier polymer and the additives used in preparation of formulations from the polymer.

Whereas polymeric materials presently being used in CR systems are assumed to be inert and thus show little or no change in the environment, this assumption is not warranted by the data accessible to this search team.

The type of data needed has simply not been generated, and that from simple laboratory toxicological evaluations is not enough. Safety cannot be based on the fact that the nature of the hazard is unknown or that no environmental contamination problem has arisen to date.

The basic unresolved questions can be categorized as follows:

(1) Nature and environmental impact of polymeric breakdown products.

(2) Nature of the interactions of polymer/agent/additives systems within a given natural environment.

(3) Impact of the various additives used.

3. Test Methods

At this time polymers are not subjected to test conditions that would reasonably allow any inference to be drawn on the expected environment impact. Polymers are tested to determine the impact of the environment on them and not vice versa. Therefore testing procedures ought to be developed that would permit a reasonable assessment of the impact of a given polymer/additive system on the environment.

4. Plan of Action

It is recognized that polymeric substances used in controlled release applications may have hitherto unknown effects on the environment. Tests assessing the nature and degree of hazard ought to be established that will permit regulatory agencies to evaluate and register commercial formulations.

It is thus recommended that the Environmental Protection Agency undertake the following steps in order to fulfill its prime mission in protecting the environment, registering improved pest control methods, and importantly, guiding industry and consumers towards the development and use of nonpersistent pesticides in nonhazardous controlled release systems wherein the environmental impact potential is less than that observed with conventional pesticide usage.

In order to meet the above objectives it is believed that the following program be undertaken both as an internal mission and through extramural activities.

1. Develop a repository of information regarding current and projected controlled release pesticide endeavors.

2. Assist outside groups and agencies in the assessment of the feasibility of controlled release pesticide usage through the sponsorship of pilot programs.

The authors believe that the established pesticide manufacturing industry will, as a rule, not undertake the development of CR pesticides because this action will almost certainly decrease the sale of pesticides. However, experience has shown that smaller entrepreneurs will undertake such efforts in order to enter a somewhat restricted market through quality competition.

3. Sponsor and/or encourage programs keyed to the development of test procedures that will determine the fate of polymers in the environment.

From examination of the literature, contact with individuals engaged in the CR pesticide area, and the past 12 years of laboratory effort by the senior author it is firmly believed that the use of the controlled release technique will greatly ameliorate the current and foreseeable environmental impact of pest control agents and plant nutrients. Furthermore, the CR methodology is probably feasible in many untried areas, will permit the use of nonpersistent agents, will usually be of greater economy, and will substantially reduce the risk of injury to handling personnel. The major potential disadvantage lies in our lack of knowledge concerning the ultimate fate of the matrix or membrane polymer.

Therefore a program ought to be developed keyed to the elucidation of polymer breakdown, residues, metabolites, etc., and the toxicological nature of such materials, under environmental conditions.

REFERENCES**

1. Baker, R. W., Lonsdale, H. K. and Gale, R. M., Membrane-Controlled Delivery Systems, Rep. No. 40, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

2. Desai, S. J., Simonelli, A. P. and Higuchi, W. I., Investigation of Factors Influencing Release of Solid Drug Dispersal Systems in Inert Matrices, J. Pharm. Sci. 54, 1459, 1965.

3. Roseman, T. J. and Higuchi, W. I., Release of Medroxyprogesterone Acetate from a Silicone Polymer, J. Pharm. Sci. 59, 353, 1970.

4. Harris, F. W., Theoretical Aspects of Controlled Release, Rep. No. 8, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

5. Collins, R. L., A Theoretical Foundation for Controlled Release, Rep. No. 9, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

6. Collins, R. L. and Doglia, S., Concentration of Pesticides Slowly Released by Diffusion, Weed Sci. 21, 343, 1973.

7. Collins, R. L., Doglia, S., Mazak, R. A. and Samulski, E. T., Controlled Release of Herbicides - Theory, Weed Sci. 21, 1, 1973.

8. Kanakkanatt, S. V., Cumulative Effects of Matrix Properties on the Diffusion Coefficients of Liquids in Rubber, International Union of Pure and App. Chem. Symp., Aberdeen, Scotland, September 1973.

9. Kanakkanatt, S. V., Theoretical Aspects of Diffusion of Molluscicides in Rubber, Rep. No. 10, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

10. Allan, G. G. and Neogi, A. N., Diffusion from Solid Polymeric Solutions Rep., Dept. Chem. Eng., University of Washington, Seattle, Wash., 1972.

11. Allan, G. G., Chopra, C. S., Neogi, A. N. and Wilkins, R. M., Design and Synthesis of Controlled Release Pesticide - Polymer Combinations, Nature (London), 234, 349, 1971.

**All references to proprietary information of manufacturers has been deleted.

12. Chandrasekaran, S. K., Baker, R. W., Buckles, R. G. and Michaels, A. S., A Mathematical Analysis for Controlled Delivery of Agrichemicals, Rep. No. 11, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

13. Furmidge, C. G. L., Hill, A. C., and Osgerby, J. M., Physico-Chemical Aspects of the Availability of Pesticides in the Soil I. Leaching of Pesticides from Granular Formulations, J. Sci. Food, Agric. 17, 518, 1966.

14. Bille, S., Mansdorf, S. F. and Cardarelli, N. F., Development of Slow Release Herbicide Materials for Controlling Aquatic Plants, Final Rep. of the University of Akron, Akron, OH, to Dept. Army office of the Chief Engineer, Wash., D.C., DACW 73-70-C-0030, July 1971.

15. Janes, G. A. and Cardarelli, N. F., Aquatic Herbicides Chronicity Study. Final Rep. of the Creative Biology Lab., Barberton, OH, to Dept. Army office of the Chief Engineer, DACW 73-73-0042, November 1973.

16. Janes, G. A., Chronicity Phenomenon, Rep. No. 14, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

17. Branum, E. A. and Bille, S. M., Pest Control Through Chronic Intoxication, Proc. Institute of Environmental Sci., 241, 1972.

18. Cardarelli, N. F., Slow Release Herbicides, Weeds, Trees & Turf 11(5), 16, 1972.

19. Cardarelli, N. F., Slow Release Molluscicides and Related Materials, in Molluscicides in Schistosomiasis Control. ed. T. C. Cheng, pp. 177-240, Academic Press, N.Y., 1974.

20. Cardarelli, N. F., Microenvironmental Evaluation of Slow Release Molluscicides, Rep. No. 29, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

21. Evans, E. S., Nelson, J. H., Pennington, N. E. and Young, W. W., Larvicidal Effectiveness of a Controlled Release Formulation of Chlorpyrifos in a Woodland Pool Habitat, Mosq. News 35(3), 343, 1975.

22. Nelson, L. L., Miller, T. A. and Young, W. W., Polymer Formulations of Mosquito Larvicides V. Effects of Continuous Low Level Chlorpyrifos Residues on the Development of Culex Pipiens Quinquefasciatus Say Populations in the Laboratory., Mosq. News 33, 396, 1973.

23. Cardarelli, N. F., Hypothesis Concerning Chronic Intoxication of Aquatic Weeds, Proc. Controlled Release Pesticide Symp., Wright State University, Dayton, OH, pp. 349-357, September 8-10, 1975.

24. Shaw, W. C., Hilton, J. L., Moreland, D. E., and Jansen, Y.Y., Herbicides in Plants, in The Nature and Fate of Herbicides Applied to Soils, Plants and Animals, ARS 20-9, Symp., U.S. Dept. Agric., Beltsville, MD, p. 119, April 27-29, 1960.

25. Dinman, B. D., "Non-Concepts" of "No-Threshold": Chemicals in the Environment, Science 175, 495, 1972.

26. Cardarelli, N. F., Controlled Release Pesticide Formulations, CRC Press, Cleveland, OH, 1976.

27. Cardarelli, N. F. and Neff, H. F., Compositions de Preservation Contre le Incrustations Sous-marines France Patent 1,506,704, 1967.

28. Cardarelli, N. F., Antifouling Elastomeric Coatings, Amer. Institute of Aeronautics and Astronautics Mtng., Naval Ordinance Plant, Forest Park, IL, February 28-March 1, 1966.

29. Cardarelli, N. F., Born, J. W. and Stockman, C. H., Marine Fouling Prevention by Sheet Rubber, Rep. (Unpublished), Natl. Assoc. Corrosion. Engr. Symp., Honolulu, Hawaii, November 8-10, 1965.

30. Bollinger, E. H., Controlled Release Antifouling Rubber Coating, Rep. No. 19, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

31. Anon, "NoFoul": Technical Background, B. F. Goodrich Co. Aerospace and Defense Div., Akron, OH, January 1969.

32. Wuerzer, D. R., Senderling, R. L. and Cardarelli, N. F., Protecting Buoys with Antifouling Rubber Coatings, Rubber World, 157(2), 77, November 1967.

33. Cardarelli, N. F. and Caprette, S. J., Antifouling Covering, U.S. Patent 3,426,473, 1969.

34. Woodford, J. M. D., Underwater Marine Coatings: Part II; Marine Biocidal Rubbers Containing Organotin Toxics., Rep. No. 496, Defence Standards Lab. Maribyrnong, Victoria, Australia, March 1972.

35. de Forest, A., Peters, R. W. and Phillip, A. T., Underwater Marine Coatings: A Detailed Examination of Elastomeric Antifouling Materials After Marine Immersion, Rep. 589, Defence Standards Lab., Maribyrnong, Victoria, Australia, May 1974.

36. Engelhart, J., Beiter, C. and Freiman, A., Recent Developments in Slow Release Organotin Antifoulants, Rep. No. 18, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

37. Carr, D. S., Organolead Lead Antifouling Paints, Rep. No. 20, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

38. Phillip, A. T., Modern Trends in Marine Antifouling Paint Research, Progress Organic Coatings (Belgium), 2, 159-192, 1973/1974.

39. Kanakkanatt, S. V., Patnode, P. P. and Cardarelli, N. F., Molluscicidal Rubber, (Unpub. Rep.) XXlll International Congress of Pure and Applied Chem., Boston, MA, July, 1971.

40. Carr, D. S. and Kronstein, M., Mechanism of Antifouling Paints, Modern Coatings, 65(12), 23, December 1975.

41. Kronstein, M., Promising New Antifoulant: Organolead-Elastomeric Coatings, Paint & Varn. Prod., 63(10), 47, October 1973.

42. Akagane, K. and Matsuo, M., Long Term Protection I. Effects of Toxic Polymers on Long Term Protection, Shikizai Kyokaishi, 45(2), 29, 1972.

43. Dyckman, E. J., Montemarano, J. A. and Fischer, E. C., Environmentally Compatible Antifouling Materials: Organometallic Polymers, Naval Eng. J., 85, 33, December 1973.

44. Montemarano, J. A. and Dyckman, E. J., Biologically Active Materials Exhibiting Controlled Release Mechanisms for Fouling Prevention, Rep. No. 21, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

45. Montemarano, J. A. and Dyckman, E. J., Performance of Organometallic Polymers as Antifouling Materials, Amer. Chem. Soc. Mtng. Rep., Los Angeles, CA, 34(1), 607, April 1974.

46. Dunn, P. and Oldfield, D., A New Concept in Antifouling Elastomers, Rep. 3rd. Australian Rubber Tech. Convention, (Australasian Institute Rubber Industry), Terrigal, N.S.W., Australia, September 18-21, 1974.

47. Hoeffler, D. F., Cercarial Dermatitis, Arch. Environ. Hlth., 29, 225, 1974.

48. Newton, M. E. and Fetterolf, C. M., Experimental Use of Bayluscide for Control of Swimmers Itch, Rep. State of Michigan Water Resources Commission, Dept. of Conservation, 1967.

49. Seeburger, D. J., Swimmers Itch Control Program. 1969 Annual Rep. Michigan Water Resources Commission, Dept. of Natural Resources, 1970.

50. Ritchie, L. S. and Malek, E. A., Molluscicides: Status of Their Evaluation and Method of Application, Wrld. Hlth. Org. Rep. Ser., PD/MOL/69.1, 1969.

51. Hopf, H. S. and Duncan, J., The Molluscicidal Properties of Organotin and Organolead Compounds, Wrld. Hlth. Org. Rep. Ser., MOL/INF/66.21, V11-1, 1966.

52. Floch, H., Deschiens, R. and Floch, T., Sur les Proprietes Molluscicides de L'oxyde et de L'acetate de Tributyl-etain, Bull. Soc. Pathol. Exot., 57, 454, 1964.

53. Floch, H. and Deschiens, R., Etude Comparee de L'action Molluscide de 5,2'-dichloro-4-nitro-salicylanilide (Bayer 73) et de Sels (Acetate et Chlorure) de Triphenyl-etain, Bull. Soc. Pathol. Exot., 55, 816, 1962.

54. Deshiens, R. and Floch, H. Donnees Complementaires sur L'action Molluscicide Remanente de Sels de Triphenyl-etain., Bull. Soc. Pathol. Exot., 56, 22, 1963.

55. Berrios-Duran, L. A., Ritchie, L. S., and Wessel, H. B., Field Screening Tests on Molluscicides Against Biomphalaria glabrata, Bull. Wrld. Hlth. Org. 39, 316, 1968.

56. Deschiens, R., Brottes, H. and Mvogo, L., Application Sue Le terrain au Cameroun, dans La Prophylaxie des Bilharzioses de L'action Molluscicides de L'oxyde de Tributyl-etain, Bull. Soc. Pathol. Exot., 59, 968, 1966.

57. Freiberg, A. H., Tributyltin Molluscicides, U.S. Patent 3,439,098, 1969.

58. Schraufstatter, E. and Gonnert, R., Method of Combatting Gastropods, U.S. Patent 3,079,297, 1963.

59. Struffe, R., Schraufstatter, E. and Gonnert, R., Alkanolamine Salts of Salicylanilides and process for their Production, U.S. Patent 3,113,067, 1963.

60. Anon., Meeting of Directors of Collaborating Laboratories on Molluscicide Testing and Evaluation, 31 Aug.-4 Sept. 1970, Wash., D.C., Wrld. Hlth. Rep. Ser., WHO/SCHISTO/71.6, 1971.

61. Cardarelli, N. F., Method for Dispersing Toxicants to Kill Disease-Spreading water-spawned Larva, Trematodes, Mollusks and Similar Organisms, and Products used in Such Methods, U.S. Patent 3,417,181, 1968.

62. Cardarelli, N. F., Biologically Active Rubber, Unpublished Rep. to Amer. Chem. Soc., Elastomer and Plastic Gp., New Eng. Section (A.D. Little Research Center, Cambridge, MA) January 14, 1969.

63. Cardarelli, N. F., Slow Release Molluscicides: Preliminary Information, Miscellaneous Rep. 72-2 of the Creative Biology Lab., Barberton, OH, October 15, 1972.

64. Cardarelli, N. F., Biocidal Elastomeric Compositions and Methods for Dispersing Biocides Therewith, U.S. Patent 3,851,053, 1974.

65. Cardarelli, N. F., Methods of Controlling the Gastropod Vectors of Parasitic Flukes, U.S. Patent 3,767,809, 1973.

66. Cardarelli, N. F., Development and Evaluation of Controlled Release Molluscicides, Annual Rep. Creative Biology Lab., Barberton, OH, to Wrld. Hlth. Org., Geneva, Switzerland, Ref. B2/181/62, March 15, 1975.

67. Engelhart, J., Slow Release Organotin Molluscicides - A New Approach to Schistosomiasis Control, Rep. of the M & T Chemical Co., Rahway, N.J., 1974.

68. Cardarelli, N. F. and Lancaster, L. L., A Preliminary Study of Copper Sulfate in Potential Slow Release and Bait Molluscicides, Rep. of the Creative Biology Lab., Barberton, OH, to International Copper Research Assoc., New York, N.Y., December 31, 1971.

69. Walker, K. E. and Cardarelli, N. F., Development of Slow Release Copper Sulfate as a Molluscicide, Annual Rep. of the Creative Biology Lab., Barberton, OH, to International Copper Research Assoc., New York, N.Y., INCRA Proj. 203, July 1, 1973.

70. Walker, K. E. and Cardarelli, N. F., Development of Slow Release Copper Sulfate as a Molluscicide, Annual Rep. Creative Biology Lab., Barberton, OH, to International Copper Research Assoc., New York, N.Y., INCRA Proj. 203, July 1, 1974.

71. Cardarelli, N. F., Development and Testing of Molluscicidal and Cercariacidal Formulations, Annual Rep. of the Creative Biology Lab. to Wrld. Hlth. Org., Ref. B2/18/62, January 30, 1974.

72. Upatham, E. S. and Christie, J. D., Laboratory Trials of Copper and TBTO Slow Release Compounds, Controlled Release Molluscicides Newsl., University of Akron, Akron, OH, 1,2, 1975.

73. Souza, da. C. P. and Paulini, E., Laboratory and Field Evaluation of Some Biocidal Rubber Formulations, Wld. Hlth. Org., WHO Rep. Ser., PD/MOL/69.9, 1969.

74. Shiff, C. J., Yiannakis, C. and Evans, R. C., Further Trials with TBTO and Other Slow Release Molluscicides in Rhodesia, Proc. Controlled Release Pesticide Symp., Wright State University, Dayton, OH, pp. 177-188, September 8-10, 1975.

75. Santos, A., Summary of Results of Laboratory Screening of Compound 443A Against O. Quadrasi, Controlled Release Molluscicides Newsl., University of Akron, Akron, OH, 1,4, 1975.

76. Hopf, H. S. and Goll, P. H., Biocidal Rubber: A Two Year Assessment of the Organotin - Containing Formulations, Rep. Tropical Pesticide Research Head Quarters, Ministry of Overseas Dev., London, U.K., July 1970.

77. Fenwick, A., Laboratory Evaluation of Biocidal Pellets 633B for Molluscicide Use, Misc. Rep. 676, Tropical Pesticide Research Institute, Arusha, Tanzania, 1969.

78. Fenwick, A., Some Observations on Molluscicides in Connexion with the Schistosomiasis Pilot Control and Training Project at Misungwi (Tanzania), Wrld. Hlth. Org. Rep. Ser., AFR/BILHARZ/14, 3 February 1969.

79. Shiff, C. J. and Yiannakis, C., Controlled Release Molluscicide Studies, Controlled Release Molluscicides Newsl., University of Akron, Akron, OH, 1,3, 1975.

80. Shiff, C. J., Focal Control of Schistosome-Bearing Snails Using Slow-Release Molluscicides, pp. 241-248 in Molluscicides in Schistosomiasis Control, ed. T. C. Cheng, Academic Press, N.Y., 1974.

81. Mansoori, A., Brief Summary of Study on MT-IE Slow Release Molluscicide, Controlled Release Molluscicides, Newsl. University of Akron, Akron, OH, 1,2, 1975.

82. Castleton, C. W., Brazilian Field Trials of MT-1E, Prog. Rep. 2, Centro de Pesquisas de Produtos Naturias, Univ. Fed. do Rio de Janeiro, Rio de Janeiro, Brasil, 1973.

83. Gilbert, B., Leme, L. A. P., Ferreira, A. M., Bulhoes, M. S., and Castleton, C., Field Tests of Hexabutyl distannoxane (TBTO) in Slow-Release Formulations Against Biomphalaria spp. Bull. Wrld. Hlth. Org. 49, 633, 1973.

84. Cardarelli, N. F., Effects of Ultralow Molluscicides Dosages on Biomphalaria glabrata and Lebistes reticulatus in Micro-Ecological Systems, Rep. No. 1, Engineering and Science Division, Community & Technical College, University of Akron, Akron, OH, August 22, 1973.

85. Anon., Bayluscide Technical Bull., Chemagro Corp., Kansas City, MO, January 1971. (EPA Reg. No's 3125-219 and 3125-218).

86. Cardarelli, N. F., Effects of Ultralow Molluscicide Dosages on Biomphalaria glabrata and Lebistes reticulatus, Rep. No. II, Engineering & Science Division, Community & Technical College, University of Akron, Akron, OH, October 1973.

87. Meyling, A. H. and Pitchford, R. J., Physico-chemical Properties of Substances Used as Molluscicides: Precipitation and Absorption, Bull. Wrld. Hlth. Org. 34, 141, 1966.

88. Cardarelli, N. F., Controlled Release Molluscicide Activity Through an Intervening Soil Barrier, Product Development Lab., University of Akron, Akron, OH, January 2, 1975.

89. Walker, K. E. and Cardarelli, N. F., Chronic Effects of Ultralow Toxicant Concentrations, Product Development Lab. Rep. Ser. to Nat. Inst. Hlth. (U.S.) Contract No. 11861-01A1, Quart. Rep. I, August 1, 1975, Quart Rep. II, November 1, 1975.

90. Gilbert, B., Leme, L. A. P., Benson, W. and Figueiredo, M., Slow Release in Tropical Disease Control, Rep. No. 4, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

91. Walker, K., Field and Laboratory Tests of Some New Molluscicides and some Novel Formulations of Existing Ones, Fifth Rep., Research & Control Dept., Castries, St. Lucia, pp. 104-106, February 1971 - February 1972.

92. Sturrock, R. F., Persistence of the Molluscicide Bayluscide (clonitralide) Emulsifiable Concentrate on Mud Surfaces in the Tropics, Ann. Trop. Med. Parasitol., 68, 427, 1974.

93. Paulini, E. and da Souza, C. P., Influence of Different Suspended Solids in Water Upon Molluscicide Activity, Wrld. Hlth. Org. Rep. Ser. PD/MOL/70.12, 1970.

94. Meredith, R., The Effect of Mud Particles on the Molluscicide Activity of the Ethanolamine Salt of 5,2'dichloro-4-nitro-salicylic Anilide, Wrld. Hlth. Org. Rep. Ser., WHO/SCHISTO/71.14, 1971.

95. Souza, C. P. and Paulini, E., Aborcao de Molluscicida Pelo Carbornate de Calcio, Rev. Brasil. de Malariol. e Doencas Trop., 21, 799, 1969.

96. Souza, C. P. and Paulini, E., Influencia de Material en Suspensao Sobre a Toxidez de Alguns Molscicides, Rev. Brasil, de Malariol, e Doencas Trop., 20, 155, 1968.

97. Etges, F. J., Bell, E. J., and Gilbertson, D. E., Bacterial Degradation of Some Molluscicidal Chemicals, Am. J. Trop. Med. Hyg., 14, 846, 1965.

98. Bell, E. J., Etges, F. J. and Jennelle, L. J., The Identity and Source of a Molluscicide-degrading Bacterium, Am. Trop. Med. Hyg., 15, 539, 1966.

99. Pellegrino, J., Univ. Fed. de Minas Gerais, Belo Horizonte, Brasil, Pers. Corres. to N. Cardarelli, University of Akron, Akron, OH, January 31, 1975.

100. Amin, M. A., Evaluation of Incracide E-51 Against *Biomphalaria Pfeifferi* and *Bulinus truncatus*, Controlled Release Molluscicides Newsl., University of Akron, Akron, OH, 1,5, 1975.

101. Cardarelli, N. F., Development and Testing of Molluscicidal and Cercariacidal Formulations, Final Rep. 1972, Creative Biology Lab. to Wrld. Hlth. Org., January 3, 1973.

102. Nestel, G. K. and Albright, F. R., Chemistry of Copper in Water Annual Rep., Lancaster Labs., Lancaster, PA, to International Copper Research Assoc., INCRA Proj. 177A, August 9, 1973.

103. Cheng, T. C. and Sullivan, J. T., Biological Studies on Copper Containing Molluscicides, Annual Rep. Institute Pathiobiology, Lehigh University, Bethlehem, PA, to International Copper Research Assoc., INCRA Proj. 193, June 30, 1974.

104. Passow, H., Rothstein, A., and Clarkson, T. W., The General Pharmacology of the Heavy Metals, Pharmacol. Rev. 13, 185, 1961.

105. Cheng, T. C. and Sullivan, J. T., Biological Studies on Copper Containing Molluscicides, Quart. Rep., Institute Pathiobiology, Lehigh University, Bethlehem, PA, to International Copper Research Assoc., INCRA Proj. 193, July 1 - September 30, 1974.

106. Fitzgerald, G. P., Factors Affecting the Toxicity of Copper to Algae and Fish, Am. J. Bot., 50, 629, 1963.

107. Hess, E. H. and Albright, F. R., Chemistry of Copper in Water, Annual Rep., Lancaster Lab. Inc., Lancaster, PA, to International Copper Assoc., N.Y., INCRA Proj. 177C, October 15, 1975.

108. McLeay, D. J., Biological Effects of Copper in Water, British Columbia Research, Vancouver, B.C., Annual Rep. to International Copper Research Assoc., New York, N.Y., INCRA Proj. 126B, January 1 - December 31, 1970.

109. Cheng, T. C., Sullivan, J. T. and Arndt, R. J., Biological Studies on Copper Containing Molluscicides, Ann. Rep., Institute Pathiobiology, Lehigh University, Bethlehem, PA, to International Copper Research Assoc., New York, N.Y., INCRA Proj. 193, June 30, 1973.

110. Cheng, T. C. and Sullivan, J. T., Biological Studies of Copper Containing Molluscicides, Annual Rep., Institute Pathiobiology, Lehigh University, Bethlehem, PA, to International Copper Research Assoc., New York, N.Y., INCRA Proj. 193, June 30, 1972.

111. Cheng, T. C. and Sullivan, J. T., A New Method For The Preliminary Testing of Chemical Molluscicides, Wrld. Hlth. Org. Rep. Ser., WHO/SCHISTO/73.27, 1973.

112. Koltnow, M., Walker, K. E. and Cardarelli, N., Destruction of Aquatic Snails By Means of a Bait Concept, Wrld. Hlth. Org. Rep. Ser., PD/MOL/69.6, 1969.

113. Anon., Development of Chemical Control For Marine Snails, Mo. Rep. Ser., Bureau Commercial Fisheries, Contract No. 14-17-0002-353, University of Akron, Akron, OH, February - July 1969.

114. Quinn, S. A., Walker, K. E. and Cardarelli, N. F., A Bait Method of Destroying Oncanelania and Biomphalaria glabrata, Snail Hosts of Schistosomiasis, and Related Studies, Annual Rep., to U.S. Army Medical Research & Development Command, Contract No. DADA-17-69-C-9166, University of Akron, Akron, Ohio, July 1 - June 30, 1970.

115. Anon., Development and Testing of Molluscicidal and Cercariacidal Formulations, Annual Progress Rep., Creative Biology Lab., Barberton, OH, Wrld. Hlth. Org., Jan. 26, 1972.

116. Cardarelli, N. F., A Method of Destroying Snail Vectors of Schistosomiasis, Final Rep., University of Akron, Akron, OH, to Rockefeller Foundation, New York, N.Y., November 10, 1969.

117. Walker, K. E., Quinn, S. A. and Bille, S. M., Development of a Toxic Bait for Destruction of Biomphalaria glabrata and other Snail Vectors of Schistosomiasis, Final Rep. Product Development Lab., University of Akron, Akron, OH, to Natl. Inst. Hlth., Contract No. NIH-70-2273, December 20, 1971.

118. Walker, K. E., Development and Field Evaluation of Frescon Baits, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

119. Bille, S. M., Walker, K. E. and Cardarelli, N. F., Field Tests of Molluscicidal Baits, Final Rep., Creative Biology Lab., Barberton, OH, to U.S. Army Medical Research & Development Command, Contract No. DADA 17-72-G-9351, 1 October 1971 - 19 December 1971.

120. Bille, S. M., Walker, K. E. and Cardarelli, N. F., A Bait Method of Destroying Oncomelania and Biomphalaria glabrata, Snail Hosts of Schistosomiasis and Related Studies, Annual Rep. II, University of Akron, Akron, OH, to U.S. Army Research & Development Command, Contract No. DADA 17-69-C-9166, 1 July 1970 - 30 June 1971.

121. Cardarelli, N. F., New Approaches to Interrupting the Schistosomiasis Transmission Cycle, Rep. to Joint Conf. on Filiariasis and Schistosomiasis, U.S.-Japan Cooperative Medical Science Program, Natl. Inst. Hlth., Bethesda, MD, July 26-28, 1971.

122. Cardarelli, N. F., Cercariacidal Potency of Slow Release Molluscicides, Rep. No. 39, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

123. Cardarelli, N. F., Bioactive Polymers, Summary Report, B. F. Goodrich Co. Aerospace & Defense Products Division, Akron, OH, 1968.

124. Anon., Pest Control with Minimal Environmental Contamination Through the Use of Slow Release Biocides, Misc. Rep. 72-1, Creative Biology Lab., February 14, 1972.

125. Lopez, V. A. and Ritchie, L. S., The Release of TBTO and Other Toxicants From Elastomers as Measured by Bioassay, Rep. No. 38, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

126. Ritchie, L. S., Lopez, U. A. and Cora, J. M., Prolonged Applications of an Organotin Against *Biomphalaria glabrata* and *Schistosoma Mansoni*, Rep. Puerto Rico Nuclear Center, San Juan, P.R., 1974.

127. Walker, K. E. and Twigg, B. A , Target Biocides for the Control of Trematode Cercaria, Abs. 1.1, p. 1, 79th Annual Mtng. Ohio Academy of Science, Wittenberg University, OH, April 17, 1970.

128. Kanakkanatt, S. V., Schistosomiasis Control By Slow-Release Molluscicides (I) Final Rep. Product Development Lab., University of Akron, Akron, OH to Wld. Hlth. Org. B2/181, September 15, 1972.

129. Anon., Laboratory Bioassay of Various Biocidal Rubbers as Mosquito Larvicides, Prelim. Rep. U.S. Army Environmental Hygiene Agency, Proj. 31-3-67/68 (Subtask 1), Edgewood Arsenal MD, 26 January 1968.

130. Boike, A. H. and Rathburn, C. B., An Evaluation of Several Toxic Rubber Compounds as Mosquito Larvicides, Mosq. News 33, 501, 1973.

131. Cardarelli, N. F. and Jackson, D. L., Slow Release Organotin Larvicides, Presented to Entomological Soc. Am., Dallas Mtng., December 2-5, 1968.

132. Cardarelli, N. F. and Hess, J. C., Floating Larvicide, U.S. Patent 3,590,119, 1971.

133. Cardarelli, N. F. and Neff, H. F., Biocidal Elastomeric Compositions, U.S. Patent 3,639,583, 1972.

134. Schultz, H. A. and Webb, A. B., Laboratory Bioassay of Pesticide - Impregnated Rubber as a Mosquito Larvicide, Mosq. News 29, 38, 1969.

135. Meltzer, Y. L., *Hormonal and Attractant Pesticide Technology*, Noyes Data Corp. Pub., Park Ridge, N.J., 1971.

136. Menn, J. J. and Pallos, F. M., Development of Morphogenetic Agents in Insect Control, Environ. Ltrs., Stauffer Chem. Co., Mt. View Calif., Aug. 13, 1974.

137. Post, L. C. and Vincent, W. R., A New Insecticide Inhibits Chitin Synthesis, Naturwis., 60, 431, 1973.

138. Chodnekar, M. S., Pfiffner, A., Rigassi, N., Schweiter, U., and Suchy, M., Insecticidal Pyrethrins in Combination with Juvenile Hormones, U.S. Patent 3,839,562, 1974.

139. Cruickshank, P. A., Some Juvenile Hormone Analogs: A Critical Appraisal, Mtterl., Schweizerischen Entomol. Gesells, 44(1,2), 7, 1971.

140. Henrick, C. A. and Siddall, J. B., Insect Control Agents, U.S. Patent 3,737,450, 1973.

141. Noguchi, Y. and Ohtaki, T., Difference in the Susceptibility of Culex Larvae Against Methoprene and Its Slow Release Formulation A Against Various Stages of the Development, Japan. J. Saint. Zool. (Eisei Dobtusu), 25(2), 185, 1974.

142. Dunn, R. L. and Strong, F. E., Control of Catch-Basin Mosquitoes Using Zoecon ZR515 Formulated in a Slow Release Polymer - A Preliminary Report, Mosq. News 33, 110, 1973.

143. Rathburn, C. B. and Boike, A. H., Laboratory and Small Plot Field Tests of Altosid and Dimiltin For the Control of Mosquito Aedes Taeniorhynchus and Culex Nigripalpus, Mosq. News 35, 540, 1975.

144. Graves, T., Formulation of Third Generation Pesticides, presented in Ways to Increase The Efficiency and Minimize the Hazards of Pesticides through Application Techniques or Formulations, Workshop Fed. Working Group on Pest Management, National Agriculture Library, Beltsville, MD, April 30 - May 1, 1975.

145. Hoffman, L. J., Ross, J. H. and Menn, J. J., Metabolism of 1-(4-Ethylphenoxy)-6,7-epoxy-3,7-dimethyl-2-octene (R20458) in the Rat., J. Agriculture Food Chem. 21, 156, 1973.

146. Gill, S. G., Hammock, B. D. and Casida, J. E., Mammalian Metabolism and Environmental Degradation of the Juvenoid 1-4'-(Ethylphenoxy)-3,7-dimethyl-6,7-epoxy-trans-2-octene and Related Compounds, J. Agriculture Food Chem. 22, 386, 1974.

147. Brown, T. M. and Brown, A. W. A., Experimental Induction of Resistance to Juvenile Hormone Mimic, J. Econ. Entomol., 67, 799, 1974.

148. Cerf, D. C. and Georghiou, G. P., Evidence of Cross Resistance to a Juvenile Hormone Analogue in Some Insecticide - Resistant Houseflies, Nature (London) 239, 401, 1972.

149. Vinson, S. B. and Plapp, F. W., Third Generation Pesticides: The Potential for Development of Resistance by Insects, J. Agriculture Food Chem., 22, 356, 1974.

150. Barnes, W. W. and Webb, A. B., A Field Evaluation of Abate Briquettes in Woodland Pools, Mosq. News, 28, 458, 1968.

151. Miles, J. W. and Woehst, J. E., Formulations for Controlled Release of Abate in Water, Advances Chem. Ser. 86, 183, 1969.

152. Whitlaw, J. T. and Evans, E. S., Selected Plastic Formulations for Use as Mosquito Larvicides, J. Econ. Entomol. 61(4), 889, 1968.

153. Nelson, L. L., Barnes, W. W., Harris, F. W. and Lawson, M. A., Evaluation of Release Rates of Dursban from Polyvinyl Chloride Formulations, J. Econ. Entomol. 63, 1870, 1970.

154. Hurlbert, S. H., Mulla, M. S., Keith, S. O., Westlake, W. E. and Dusch, M. E., Biological Effect and Persistance of Dursban in Freshwater Ponds, J. Econ. Entomol. 63, 43, 1970.

155. Parker, T. A., Effectiveness of 9.9 percent Dursban in Polyethylene Applied as a Pre-Season Larvicide, Special Study No. 31-005-71, U.S. Army Environmental Hygiene Agency, (AD 725,573), 1970.

156. Roberts, L. W. and Miller, T. A., Polymer Formulations of Dursban and Abate as Mosquito Larvicides, Special Study No. 31-006-71, U.S. Army Environmental Hygiene Agency, (AD 729344), 1971.

157. Nelson, L. L. and Miller, T. A., Laboratory Evaluation of Residues Maintained in Water Treated with Polyvinyl Chloride Formulations of Dursban, Special Study No. 31-008-72, U.S. Army Environmental Hygiene Agency, 1971.

158. Lawson, M. A., Miller, T. A., Oakleaf, R. J. and Young, W. W., Polymer Formulations of Mosquito Larvicides, VIII Laboratory Evaluations of Selected Polyethylene Formulations of Chlorpyrifos, Mosq. News, 33, 561, 1973.

159. Nelson, L. L. and Whitlaw, J. T., Laboratory Release Rate Studies of Diazinon and Supracide R from Polyvinyl Chloride Formulations, Special Study No. 31-019-71/72, U.S. Army Environmental Hygiene Agency, (AD 736, 422), 1972.

160. Nelson, L. L., Laboratory Release Rate Studies of Dursban - Polymeric Formulations, Special Study No. 31-007-71/72, U.S. Army Environmental Hygiene Agency, 1971.

161. Miller, T. A., Nelson, L. L., Young, W. W., Roberts, L. W., Roberts, D. R. and Wilkinson, R. N., Polymer Formulations of Mosquito Larvicides I. Effectiveness of Polyvinyl Chloride Formulations of Chlorpyrifos Applied to Artificial Field Pools, Mosq. News 33, 148, 1973.

162. Miller, T. A., Nelson, L. L. and Young, W. W., Polymer Formulations of Mosquito Larvicides, IV. Larvicidal Effectiveness of Chlorpyrifos During an 18 Month Field Test, Mosq. News 33, 172, 1973.

163. Nelson, L. L., Miller, T. A., Whitlaw, J. T., Young, W. W., and Lawson, M. A., Polymer Formulations of Mosquito Larvicides VI. Laboratory and Field Evaluation of Selected Polyethylene Formulations of Chlorpyrifos, Mosq. News 33, 403, 1973.

164. Nelson, L. L, Miller, T. A., and Young, W. W., Polymer Formulations of Mosquito Larvicides V. Effects of Continuous Low Level Chlorpyrifos Residues on the Development of Culex Pipiens Quinquefasciatus Say Populations in the Laboratory, Mosq. News 33, 396, 1973.

165. Roberts, L. W., Roberts, D. R., Miller, T. A., Nelson, L. L. and Young, W. W., Polymer Formulations of Mosquito Larvicides II. Effects of a Polyurethane Formulation of Chlorpyrifos on Culex Populations Naturally Infesting Artificial Field Pools, Mosq. News 33, 155, 1973.

166. Wilkinson, R. N., Barnes, W. W., Gillogly, A. R. and Minnemeyer, C. D., Field Evaluation of Slow Release Mosquito Larvicides, J. Econ. Entomol. 64, 1, 1973.

167. Nelson, J. H. and Evans, E. S., Field Evaluation of Larvicidal Effectiveness, Effects on Nontarget Species and Environmental Residues of a Slow Release Polymer Formulation of Chlorpyrifos, March - Oct. 1973, Special Study No. 44-022-73/74, U.S. Army Environmental Hygiene Agency, 1975.

168. Roberts, D. R., Roberts, L. W., Miller, T. A., Nelson, L. L. and Young, W. W., Polymer Formulations of Mosquito Larvicides. III. Effects of a Polyethylene Formulation of Chlorpyrifos on Non-target Populations Naturally Infesting Artificial Field Pools, Mosq. News, 33, 165, 1973.

169. Nelson, J. H., Evans, E. S., Pennington, N. E. and Young, W. W., The U.S. Army Environmental Hygiene Agency Activities in the Area of Slow-release Insecticides, Rep. No. 30, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

170. Fanger, G. O., Microencapsulation: A Brief History and Introduction, in Microencapsulation: Processes and Applications, ed. J. E. Vandegaer, Plenum Press, 1974.

171. Fogle, M. V., Microencapsulation Promises Big Potential in Agricultural Field, Croplife, February 1968.

172. Luzzi, L. A., Microencapsulation, J. Pharm. Sci. 59, 1367, 1970.

173. Anon., Microencapsulation Advances into New Areas, Chem. & Eng. News, August 12, 1974.

174. Bakan, J. A. and Anderson, J. L., Microencapsulation, in The Theory and Practice of Industrial Pharmacy, ed. Lachman, L. et al., Lea & Febiger Pub., 1970.

175. Bakan, J. A., Microcapsule Drug Delivery Systems, Polymer Sci. & Tech., Vol. 8, Polymer in Medicine and Surgery ed. Kronenthal, R. E., et al., Plenum Press, 1975.

176. Bakan, J. A. and Sloan, F. D., Microencapsulation of Drugs, Drug and Cosmetic Industry, 34, March 1972.

177. Bakan, J. A., Microencapsulation of Foods and Related Products, Food Technology 27(11), 34, 1973.

178. Ignoffo, C. M. and Batzer, O. F., Microencapsulation and Ultraviolet Protectants to Increase Sunlight Stability of an Insect Virus, J. Econ. Entomol. 64, 850, 1971.

179. Berger, B. B., Miller, C. D. and Langer, G., Electrostatic Encapsulation, U.S. Patent 3,208,951, 1965.

180. Sachsel, G. F. and Nack, H., Method of Encapsulating Liquids, U.S. Patent 3,202,533, 1965.

181. Nack, H., Fluidized Bed Coating of Fragile Bodies, U.S. Patent 3,382,093, 1968.

182. Grass, G. M. Jr., and Robinson, M. J., Apparatus for Coating Discrete Solids, U.S. Patent 3,237,596, 1966.

183. Vandegaer, J. E., Encapsulation by Interfacial Polycondensation, U.S. Patent 3,577,515, 1971.

184. Vandegaer, J. E. and Meier, F. G., Encapsulation Process, U.S. Patent 3,575,882, 1971.

185. Santo, J. E. and Vandegaer, J. E., Process for Encapsulation, U.S. Patent 3,492,380, 1970.

186. Santo, J. E. and Abend, P. G., Manufacture of Ingestible Capsules, U.S. Patent 3,607,776, 1971.

187. Vandegaer, J. E. and Meyer, F. G., Process for Encapsulation, U.S. Patent 3,464,926, 1969.

188. Jolkovski, R. M. and Powers, D. H., Method for Making Capsules by Interfacial Polymerization, U.S. Patent 3,270,100, 1966.

189. Hiestand, E. N., Wagner, J. G. and Knoechel, E. J., Coating by Phase Separation, U.S. Patent 3,242,051, 1968.

190. Jensen, E. H., Coating by Phase Separation, U.S. Patent 3,265,629, 1966.

191. Miller, R. E., Fanger, G. O. and McNiff, R. G., Union South Africa, Patent 4211-66, 1967.

192. Brynko, C. and Olderman, G. M., Replacement of Capsule Contents by Diffusion, U.S. Patent 3,516,943, 1970.

193. Somerville, G. R., Method for Mass Producing Small Spherical Particles, U.S. Patent 3,389,194, 1968.

194. Sparks, R. E., Mason, N. S., Meier, P. M., Litt, M. H. and Linden, O., Removal of Uremic Waste Metabolites from the Intestinal Tract by Encapsulated Carbon and Oxidized Starch Trans. Am. Soc. Artificial Internal Organs 17, 229, 1971.

195. Speiser, P. P., Mikrocapseln im Nanometergrossenberich und Verfahren zu deren Herstellung, German Patent 2,360,384, 1973.

196. Sternberg, S., Bixler, H. J. and Michaels, A. S., Encapsulating Particles and Process for Making Same, U.S. Patent 3,639,306, 1972.

197. Powell, T. C., Steinle, M. E. and Yoncoskie, R. A., Process of Forming Minute Capsules En Masse, U.S. Patent 3,415,758, 1968.

198. Reyes, Z., Process of Making Microcapsules, U.S. Patent 3,173,878, 1965.

199. Bakan, J. A., Microencapsulation of Pesticides and Other Agricultural Materials, Proc. Controlled Release Pesticides Symp., 76, Wright State University, Dayton, OH, September 8-10, 1975.

200. Siebel, J., Anwendung von Schadlings Bekampungs-mitteln, German Patent 2,017,356, 1970.

201. Nemeth, H. C., Stabile Wassrige Dispersionen von Eingekapseltem Parathion, German Patent 2,309,983, 1973.

202. Fanger, G. O., What Good Are Microcapsules?, Chem. Tech., 379, July 1974.

203. Scher, H. B., Verfahren zum Einkapseln mit Wasser Nicht Mischbarer Stoffe, German Patent 2,312,059, 1973.

204. Wasti, S. S., Shaw, F. R. and Smith, C. T., Detection of Residues of Rabon in Manure of Rhode Island Red Hens, J. Econ. Entomol. 63, 1355, 1970.

205. Wasti, S. S. and Shaw, F. R. Residues of Encapsulated Rabon in Tissues and Eggs of Poultry, J. Econ. Entomol. 61, 244, 1971.

206. Wasti, S. S., Mkwaila, B. and Shaw, F., Residues of Encapsulated Rabon in Poultry Manure and Its Larvicidal Activity to House Flies, J. Econ. Entomol. 64, 225, 1971.

207. Miller, R. W., Drazek, P. A., Martin, M. S. and Gordon, C. H., Feeding of Micro-encapsulated Gardona For the Control of Fly Larvae in Cow Manure, Rep. No. 169, Ann. Mtng. Amer. Dairy Sci. Assoc., Gainesville, Fla. DCRB 70-8, June 1970.

208. Miller, R. W. and Gordon, C. H., Encapsulated Rabon for Larval House Fly Control in Cow Manure, J. Econ. Entomol. 65, 455, 1972.

209. Miller, R. W. and Beroza, M., Microencapsulated Insecticide Feed Additive for Control of Fly Larvae in Cow Manure, U.S. Patent 3,830,914, 1974.

210. Siebel, J., Formulierung von Schadlings Kampfungsmitteln German Patent 2,017,808, 1971.

211. Anon., Tiny Capsules Add New Life to Old Pesticides, Chem. Week 110, 75, June 21, 1972.

212. Anon., Pennwalt to Test Encapsulated Pesticide, Chem. Eng. News 50(23), 68, 1972.

213. Raun, E. S. and Jackson, R. D., Encapsulation as a Technique for Formulating Microbial and Chemical Insecticides, J. Econ. Entomol. 59, 620, 1966.

214. Gifford, J. R., Oliver, B. F. and Trahan, G. B., Rice Water Weevil Control with Pirimiphos Ethyl Seed Treatment, J. Econ. Entomol. 68, 79, 1975.

215. Markin, G. P., Mauffray, C. J. and Adams, D. J., A Granular Application for Very Low Volumes of Microencapsulated Insect Baits or Other Materials, Rep. U.S. Dept. Agric., Agricultural Research Service 81-34 (Vol. 81, No. 34, p. 4), October 1969.

216. Markin, G. P. and Hill, S. O., Microencapsulated Oil Bait for the Control of the Imported Fire Ant., Entomol. Soc. Annual Meeting, Dallas, Texas, December 5, 1968.

217. Markin, G. P. and Hill, S. O., Microencapsulated Oil Bait for Control of the Imported Fire Ant., J. Econ. Entomol. 64, 193, 1971.

218. Markin, G. P., Henderson, J., Collins, H. L., Dillier, J., Spence, J. and Fogel, M. V., Feasibility Studies of the Utilization of Microencapsulated Baits for Control of the Imported Fire Ant. Proj. Rep. USDA-APHIS, 1966-1972, 1972.

219. Markin, G. P., Collins, H. L. and O'Neil, J., Control of the Imported Fire Ant with Winter Applications of Microencapsulated Mirex Bait, J. Econ. Entomol. 68, 711, 1975.

220. Markin, G. P., O'Neal, J. and Collins, H. L., Control of the Red Imported Fire Ant. with Microencapsulated Baits Containing Reduced Amounts of Mirex, J. Georgia Entomol. Soc. 10(4), 281, October 1975.

221. Beard, R. L., Termite Biology and Bait-Block Method of Control, Bull. 748, Connecticut Agriculture Experimental Station, New Haven, Conn., November 1974.

222. Ennik, F., Abatement of Yellow Jackets Using Encapsulated Formulations of Diazinon and Rabon, J. Econ. Entomol. 66, 1097, 1973.

223. Beroza, M., Insect Sex Attractant Pheromones, A Tool for Reducing Insecticide Contamination in the Environment, Toxicol. & Environ. Chem. Rev. 1, 109, 1972.

224. Beroza, M., Inscoe, M. N., Schwartz, P. H., Keplinger, M. L. and Mastri, C. W., Acute Toxicity Studies with Insect Attractants, Toxicol. & Appl. Pharmacol. 31, 421, 1975.

225. McLaughlin, J. R., Mitchell, E. R. and Tumlinson, J. H., Evaluation of Some Formulations for Dispensing Insect Pheromones in Field and Orchard Crops, Proc. Controlled Release Pesticide Symp., 209, Wright State University, Dayton, OH, September 8-10, 1975.

226. Toba, H. H., Kishaba, A. N. and Wolf, W. W., A Polyethylene Bag for Dispensing the Synthetic Sex Pheromone of the Cabbage Looper, J. Econ. Entomol. 62, 517, 1969.

227. Bull, D. L., Coppedge, J. R., Hardee, D. D., Rummel, D. R., McKibben, G. H. and House, V. S., Formulations for Controlling the Release of Synthetic Pheromone (Grandlure) of the Boll Weevil, Environ. Entomol. 2(5), 905, October 1973.

228. Peacock, J. W. and Cuthbert, R. A., Field and Laboratory Evaluations of Controlled Release Dispensers for Scolytus Multistriatus Pheromone, Proc. Controlled Release Pesticide Symp. 216, Wright State University, Dayton, OH, September 8-10, 1975.

229. Inscoe, M. N. and Beroza, M. in Pest Management with Insect Sex Attractants, (pp. 145-181), M. Beroza, ed., ACS Symposium Series 23, Amer. Chem. Soc., Wash., D.C., 1976.

230. Beroza, M., Stevens, L. J., Bierl, B. A., Phillips, F. M. and Tardiff, J. G. R., Pre-and Post Season Field Tests with Disparlure, the Sex Pheromone of the Gypsy Moth, to Prevent Mating, Environ. Entomol. 2, 1051, 1973.

231. Stevens, L. J. and Beroza, M., Mating-Inhibition Field Tests Using Disparlure, the Synthetic Gypsy Moth Sex Pheromone, J. Econ. Entomol. 65, 1090, 1972.

232. Beroza, M., Bierl, B. A., Tardiff, J. G. R., Cook, D. A. and Paszek, E. C., Activity and Persistence of Synthetic and Natural Sex Attractant of the Gypsy Moth in Laboratory and Field Trials, J. Econ. Entomol. 64, 1499, 1971.

233. Beroza, M., Hood, C. S., Trefey, D., Leonard, D. E., Knipling, E. F., Klassen, W. and Stevens, L. J., Large Scale Field Trial with Microencapsulated Sex Pheromone to Prevent Mating of the Gypsy Moth, J. Econ. Entomol., 67, 659, 1974.

234. Beroza, M., Hood, C. S., Trefey, D., Leonard, D. E., Knipling, E. F. and Klassen, W., Field Trials with Disparlure in Massachusetts to Suppress Mating of the Gypsy Moth, Environ. Entomol. 4, 705, 1975.

235. Schwalbe, C. P., Cameron, E. A., Hall, D. J., Richerson, J. V., Beroza, M. and Stevens, L. J., Field Tests of Microencapsulated Disparlure for Suppression of Mating Among Wild and Laboratory-Reared Gypsy Moths, J. Environ. Entomol. 3, 589, 1974.

236. Cameron, R. A., Schwalbe, C. P., Beroza, M. and Knipling, E. F., Disruption of Gypsy Moth Mating with Microencapsulated Disparlure, Science 183 (4128), 972, March 8, 1974.

237. Granett, J. and Doane, C. C., Reduction of Gypsy Moth Male Mating Potential in Dense Populations by Mist Blower Sprays of Microencapsulated Disparlure, J. Econ. Entomol. 68, 435, 1975.

238. Cameron, E. A., Schwalbe, C. P., Stevens, L. J. and Beroza, M., Field Tests of the Olefin Precursor of Disparlure for Suppression of Mating in the Gypsy Moth, J. Econ. Entomol. 68, 158, 1975.

239. Bierl, B. A. and DeVilbiss, D., Insect Sex Attractants in Controlled Release Formulations, Proc. Controlled Release Pesticide Symp. 230, Wright State University, Dayton, OH, September 8-10, 1975.

240. Beroza, M., Paszek, E. C., DeVilbiss, D., Bierl, B. A. and Tardiff, J. G. R., A 3-Layer Laminated Dispenser of Disparlure for Use in Traps for Gypsy Moths, Environ. Entomol. 4, 712, 1975.

241. Hardee, D. D., Slow-Release Formulations for Grandlure, the Pheromone of the Boll Weevil, Rep. No. 36, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

242. McKibben, G. H., A Device for Injecting Grandlure into Cigarette Filters, J. Econ. Entomol. 65, 1509, 1972.

243. Bull, D. L., Coppedge, J. R., Ridgeway, R. L., Hardee, D. D. and Graves, T. M., Formulations for Controlling the Release of Synthetic Pheromone (Grandlure) of the Boll Weevil 1. Analytical Studies, Environ. Entomol. 2, 829, 1973.

244. Coppedge, J. R., Bull, D. L., House, V. S., Ridgeway, R. L., Bottrell, D. G. and Cowan, C. B., Formulations for Controlling the Release of Synthetic Pheromone (Grandlure) of the Boll Weevil 2. Biological Studies, Environ. Entomol. 2(5), 837, 1973.

245. Hardee, D. D., Graves, T. M., McKibben, G. H., Johnson, W. L., Gueldner, R. C. and Olsen, C. M., A Slow-Release Formulation of Grandlure, the Pheromone of the Boll Weevil, J. Econ. Entomol. 67, 44, 1974.

246. Hardee, D. D., McKibben, G. H. and Huddleston, P. M., Grandlure for Boll Weevils: Controlled Release with a Laminated Plastic Dispenser, J. Econ. Entomol. 68, 477, 1975.

247. Johnson, W. L., McKibben, G. H., Rodriguez, J. and Davich, T. B. Boll Weevil: Increased Longevity of Grandlure Using Different Formulations and Dispensers, J. Econ. Entomol., 69, 263, 1976.

248. McGovern, T. P., Beroza, M., Ohinata, K., Miyashita, D., and Steiner, L. F., Volatility and Attractiveness to the Mediterranean Fruit Fly of Trimedlure and Its Isomers, and a Comparison of its Volatility with that of Seven Other Insect Attractants, J. Econ. Entomol. 59, 1450, 1966.

249. McGovern, T. B. and Beroza, M., Effects of Fixatives and Other Chemicals in Extending the Activity of the Insect Attractant Trimedlure, J. Econ. Entomol. 60, 379, 1967.

250. Keiser, I., Kobayashi, R. M. and Harris, E. J., Enhanced Duration of Residual Effectiveness Against the Mediterranean Fruit Fly of Guava Foliage Treated with Encapsulated Insecticides and Lures, Proc. Controlled Release Pesticide Symp., 264, Wright State University, Dayton, OH, September 8-10, 1975.

251. Cunningham, R. T. and Steiner, L. F., Field Trial of Cue-Lure + Naled on Saturated Fiberboard Blocks for Control of the Melon Fly by the Male - Annihilation Technique, J. Econ. Entomol. 65, 505, 1972.

252. Bateman, M. A., Insumza, V. and Arretz, P., The Eradication of Queensland Fruit Fly from Easter Island, FAO Plant Protection Bull., 1141, 1973.

253. Harris, E. J., Controlled Release Cue-Lure Formulations For Detection and Control of the Melon Fly, Rep. No. 35, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

254. Gentry, C. R., Beroza, M., Blythe, J. L., and Bierl, B. A., Efficacy Trials with the Pheromone of the Oriental Fruit Moth and Data on the Lesser Appleworm, J. Econ. Entomol. 67, 607, 1974.

255. Fitzgerald, T. D., St. Clair, A. D., Daterman, G. E., and Smith, R. G., Slow Release Plastic Formulations of The Cabbage Looper Pheromone cis-7-Dodecenyl Acetate: Release rate and Biological Activity, Environ. Entomol. 2, 607, 1973.

256. Beroza, M., Paszek, E. C., Mitchell, E. R., Bierl, B. A., McLaughlin, J. R. and Chambers, D. L., Tests of a 3-Layer Laminated Plastic Bait Dispenser for Controlled Emission of Attractants from Insect Traps, Environ. Entomol. 3, 926, 1974.

257. McGovern, T. P. and Beroza, M., Volatility and Compositional Changes of Japanese Beetle-Attracted Mixtures and Means of Dispensing Sufficient Vapor Having a Constant Composition, J. Econ. Entomol. 3, 1475, 1970.

258. Peacock, J. W., Cuthbert, R. A., Gore, W. E., Lanier, G. N., Pearce, G. T. and Silverstein, R. N., Collection on Porapak Q of the Aggregation Pheromone of *Scolytus multistriatus*, J. Chem. Ecol. 1, 149, 1975.

259. Pearce, G. T., Gore, W. E., Silverstein, R. M., Peacock, J. W., Cuthbert, R. A., Lanier, G. N. and Simeone, J. B., Chemical Attractants for the Smaller European Elm Bark Beetle *Scolytus Multistriatus*, J. Chem. Ecol. 1, 115, 1975.

260. Peacock, J. W. and Cuthbert, R. A., Pheromone Baited Traps for Detecting the Smaller European Elm Bark Beetle, U.S. Dept. Agriculture Crop, Econ. Institute Rep. 25(24), 497, 1975.

261. Peacock, J. W., U.S. Dept. Agric. Northeast Forest Experi. Sta., Delaware, OH, correspondence to, Cardarelli, N. F., University of Akron, Akron, OH, November 20, 1975.

262. Feinberg, I., Process for Preparing a Stable Polymer Latex Containing an Insecticide, U.S. Patent 3,400,093, 1968.

263. Allan, G. G., Gara, R. J. and Wilkins, R. M., Field Testing of Insecticide-Polymer Combinations for the Long Term Control of the Mahogany Shootborer, Internat. Pest Control (London), Vol. 16, July-Aug., 1974.

264. Olton, G. S., Slow Release Formulations Show Promise, Pest Control 43(10), 20, October 1975.

265. Olton, G. S., Killmaster^{tm}: A New Controlled Release Insecticide for Cockroach Control, Proc. Controlled Release Pesticide Symp., 258, Wright State University, Dayton, OH, September 8-10, 1975.

266. DeSavigny, C. B. and Ivy, E. E., Microencapsulated Pesticides, Amer. Chem. Soc. Div. Org. Coatings & Plast. Chem. Chicago Mtng., 33(2), 554, Aug. 26-31, 1973.

267. Pass, B. C. and Dorough, H. W., Insecticidal and Residual Properties of Emulsifiable Concentrate and Encapsulated Formulations of Methyl Parathion Sprayed on Alfalfa, J. Econ. Entomol., 66, 1117, 1973.

268. Quisumbing, A. R., Lawatsch, D. J. and Kydonieus, A. F., Field Studies on the Control of the German Cockroach Blatella germanica Using HERCON^{tm} "Roach Tape" and Standard Sprays Proc. Controlled Release Pesticide Symp., 247, Wright State University, Dayton, OH, September 8-10, 1975.

269. Kydonieus, A. F. and Smith, I. K., Efficacy of Hercon^{tm} Polymeric Controlled Release Dispensers (PCRD) in Cockroach Control, Rep. Herculite Protective Fabrics Corp., New York, N.Y., 1974.

270. Kydonieus, A. F., Smith, I. K. and Hyman, S., A Polymeric Delivery System for the Controlled Release of Pesticides, Proc. Controlled Release Pesticide Symp., 60, Wright State University, Dayton, OH, September 8-10, 1975.

271. Anon., Controlled Release Insecticides, Soap/Cosmetics/Chem. Specialties, 44, March 1975.

272. Steiner, L. F., Low Cost Plastic Fruit Fly Trap, J. Econ. Entomol. 50, 508, 1957.

273. Brooks, G. D., Elmore, C. M., Schoof, H. F. and Carmichael, G. T., Field Evaluation of Three Types of DDVP Dispensers for the Control of Culex pipens quinquefasciatus Say in Catch Basins, Proc. 15th Annual Mtng. N.J. Mosq. Extermin. Assoc. & 19th Annual Mtng. Am. Mosq. Control Assoc., Atlantic City, N.J., 1963.

274. Smittle, B. J. and Burden, G. S., Dichlorvos as a Vapor Toxicant for Control of Roaches, Bedbugs, Fleas, Pest Control 33, 26, 1965.

275. Folckemer, F. B., Hanson, R. E. and Miller, A., Resin Composition Comprising Organophosphorus Pesticides, U.S. Patent 3,318,769, 1967.

276. Geiger, M. and Fuerer, R., Vapour Emissive Compositions Containing Dimethyl Dichlorovinyl Phosphate, U.S. Patent 3,364,105, 1968.

277. Aries, R., Compositions Pesticides Stabilisées, France Patent 2,105,097, 1972.

278. Aries, R., Compositions Pesticides Stabilisées, France Patent 2,112,136, 1972.

279. Aires, R., Compositions Antiparasitaires Stabilisées, France Patent 2,117,768, 1972.

280. Aries, R., Compositions Pesticides de Toxicite Reduite, France Patent 2,108,927, 1972.

281. Aries, R. Compositions Antiparasitaire Remanentes, France Patent 2,117,769, 1972.

282. Aries, R., Compositions Pesticides Stabilisées, France Patent 2,123,138, 1972.

283. Aries, R., Compositions Antiparasitaires Remanentes, France Patent 2,123,139, 1972.

284. Rabussier, B., Mandon, J. P. and Hennart, C., Verfahren zur Herstellung einer Vorrichtung zum Abgebeh von Insektiziden Dampfen und Nach Diesem Verfahren Hergestellte Verdamp Fereinheit, Switzerland Patent 526,903, 1972.

285. Rabussier, B. and Mandon, J. P., Verdampfer für Insektizide mit einer Olefin Polymerisat Permeationswandung, Luxemberg Patent (German Patent Office) 2,412,368, 1974.

286. Bogaard, T. D., Controlled Release of Vapor Forming Compounds from a New Matrix., Proc. Controlled Release Pesticide Symp., 132, Wright State University, Dayton, OH, September 8-10, 1975.

287. Nysted, L. N., Vapor Diffusing Composition and Method of Making the Same, U.S. Patent 3,745,213, 1973.

288. Soloway, S. B. and Morales, J. G., Volatile Insecticide, U.S. Patent 3,740,428, 1973.

289. Weichbrodt, M. and Sy, M. H., Feste Insektenbekampfungsmittel mit Lang Dauernder Begasungswirkung, German Patent 2,038,024, 1972.

290. Seaman, D. and Warrington, R. P., Slow Release Pirimicarb Granular Formulations: Measurements of Release Rates Under Field Conditions, Pestic. Sci. 3, 749, 1972.

291. Stokes, R. A., Coppedge, J. R. and Ridgeway, R. L., Chemical and Biological Evaluation of the Release of Aldicarb From Granular Formulations, J. Agr. Food Chem. 18, 195, 1970.

292. Davis, J. W. and Cowan, C. B., Field Evaluation of Three Formulations of Aldicarb for Control of Cotton Insects, J. Econ. Entomol. 65, 231, 1972.

293. Stokes, R. A., Coppedge, J. A., Bull, D. L. and Ridgeway, R. L., Use of Selected Plastics in Controlled Release Granular Formulations of Aldicarb and Dimethoate, J. Agr. Food Chem. 21, 103, 1973.

294. Coppedge, J. R., Stokes, R. A., Ridgeway, R. L. and Kinzer, R. E., Slow Release Formulations of Aldicarb: Modeling of Soil Persistence, USDA ARS Cotton Insects Lab., College Station, Texas, ARS Pub. #20, December 1974.

295. Geary, R. J., Pesticidal Resin and Method of Preparing Same, U.S. Patent 3,223,513, 1965.

296. McFadden, R. T., Langner, R. R., and Wade, L. L., Biocidally-active Mixed Phosphorothioate Ester-Containing and Mixed Phospheroamidate Ester - Containing Polymeric Materials, U.S. Patent 3,212,967, 1965.

297. Campbell, C. C., Pesticidal Compositions, U.S. Patent 3,740,419, 1973.

298. Allan, G. G., Chopra, C. S., Friedhoff, J. F., Gara, R. I., Maggi, M. W., Neogi, A. N., Roberts, S. C. and Wilkins, R. M., Pesticides, Pollution and Polymers, Chem. Tech. 4, 171, March 1973.

299. Farbenfabriken, Bayer Akt., Granule' Destine' a' Absorber et Dispenser un Agent Chimique pour L'agriculture et son Procédé de Preparation, France Patent 2,082,026, 1969.

300. Sjogren, R. D., Preliminary Evaluation of Capsules Containing a Chitin Synthesis Inhibitor, Proc. Controlled Release Pesticide Symp. 217, Wright State University, Dayton, OH, September 8-10, 1975.

301. Wellinga, K., Mulder, R. and Von Daalen, J. J., Synthesis and Laboratory Evaluation of 1-(2,6-disubstituted benzoyl)-3-phenylureas, A New Class of Insecticides. I. 1-(2,6-dichlorobenzoyl)-3-phenylureas, J. Agr. Food Chem. 21, 348, 1973.

302. Smith, P. and Smith, L., Organotin Compounds and Applications, Chem. in Brit. 11(6), 208, June 1975.

303. McCoy, F. C. and Swanson, C. L. W., Oil-Solubilizing Nitrogen-Containing Pesticidal Compounds, U.S. Patent 3,681,348, 1972.

304. Barnes, W. W. and Whitlaw, J. T., Preliminary Evaluation of Controlled Release Herbicide Formulations for Aquatic Weeds, Rep. U.S. Army Environ. Hygiene Agency, Edgewood, MD, (Proj. 31-004-69/70), 1970.

305. Young, W. W. and Nelson, L. L., Evaluation of Controlled Release Herbicide Formulations for Aquatic Weeds, Entomol. Spec. Study No. 31-004-69/71, U.S. Army Environment Hygiene Agency, Edgewood, MD, July 1969-July 1970.

306. Steward, K. K. and Nelson, L. L., Evaluations of Controlled Release PVC Formulations of 2,4-D on Watermilfoil, Research Planning Conf., Interagency Research Advisory Committee Aquatic Plant Control Program, Office of Chief Eng., Dept. Army, Washington, D.C., October 1970.

307. Steward, K. K. and Nelson, L. L., Evaluations of Controlled Release PVC and Attaclay Formulations of 2,4-D on Eurasian Watermilfoil, Hyacinth Control J. 10, 35, May 1972.

308. Harris, F. W., Norris, S. O. and Post, L. K., Investigation of Factors Influencing Release of Herbicides from Polymer Matrices: The Polyethylene Matrix, Quart. Rep. II, Contract No. DACW 73-71-C-0053, U.S. Army Corps Engineers, Oct. 1971-Dec. 1971.

309. Steward, K. K., Weed Investigations - Aquatic and Noncrop Areas, Annual Rep., Agricultural Research Service, Ft. Lauderdale, Fla., July 1970 - June 1971.

310. Nelson, L. L., Evaluation of Slow-Release Herbicide Formulations for Aquatic Weed Control, Rep., Entomol. Special Study No. 31-004-69/72, July 1970 - July 1971, U.S. Army Environmental Hygiene Agency, 21 January 1972.

311. Harris, F. W., Norris, S. O. and Post, L. K., Factors Influencing Release of Fenac from Polyethylene Matrices, Weed Sci. 21(4), 318-321, July 1973.

312. Harris, F. W., Controlled-Release Herbicide-Polymer Formulations for Aquatic Weed Control, Hyacinth Control J. 11, 61, June 1973.

313. Harris, F. W., Feld, W. A. and Post, L. K., Investigation of Factors Influencing Release of Herbicides from Polymers Containing Herbicides as Pendent Side Chains, Annual Rep. Contract No. DACW 73-74-C-0001, U.S. Army Office Chief Engineer, Washington, D.C., July 1973-June 1974.

314. Harris, F. W. and Post, L. K., Synthesis of Polymers Containing Aquatic Herbicides as Pendent Substituents, Rep. No. 17, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

315. Harris, F. W. and Post, L. K., Synthesis and Polymerization of the Vinyl and Acryloyloxyethyl Esters of 2,4-dichlorophenoxyacetic acid and 2-(2,4,5-trichlorophenoxy)propionic acid, J. Poly. Sci. A-1, 13, 225, 1975.

316. Harris, F. W., Feld, W. A. and Bowen, B. K., Polymers Containing pendent Herbicide Substituents, Proc. Controlled Release Pesticide Symp., 334, Wright State University, Dayton, OH, September 8-10, 1975.

317. Baltazzi, E., Alkyd Resins with Herbicidal Properties, U.S. Patent 3,343,941, 1967.

318. Bille, S., Mansdorf, S. Z. and Cardarelli, N. F., Development of Slow Release Herbicide Materials for Controlling Aquatic Plants, Ann. Rep. II., University of Akron, Product Development Laboratory, (Nov. 1969 - Sept. 1970) to Dept. Army, Office Chief Engineer, Contract No. DACW 73-70-C-0030, (AD879-356L), October 1970.

319. Bille, S. Mansdorf, S. F. and Cardarelli, N. F., Development of Slow Release Herbicide Materials for Controlling Aquatic Plants, Annual Rep. II (Nov. 1969 - July 1971) to Dept. Army Office Chief Engineer, Contract No. DACW 73-70-C-0030, University of Akron, Product Development Lab., July 1971.

320. Mansdorf, S. F., Slow Release: Development of Aquatic Herbicide Carrier Systems, Rep. No. 12, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

321. Cardarelli, N. F., Thompson, W. E. and Janes, G. A., Utilization of Rubber in Controlled Release Herbicide Applications, Rubber Developments J. 27(2), 54, 1974.

322. Thompson, W. E., Field Tests of Slow Release Herbicides, Rep. No. 15, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

323. Gangstad, E. O., Scott, R. H. and Cason, R. G., Controlled-Release Herbicides, Tech. Rep. No. 1, Aquatic Plant Control Program, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss., October 1972.

324. Cardarelli, N. F., Evaluation of Incracide E-51 Against Select Aquatic Weeds and Algae, Rep. Creative Biology Lab., Proj. 104 to International Copper Research Assoc., New York, N.Y., April 5, 1975.

325. Janes, G. A., Bille, S. M. and Cardarelli, N. F., Development and Evaluation of Controlled Release Herbicides, Quart. Rep. U.S. Army Corps Engineers Contract No. DACW 39-76-C-0029, Oct. 1 - Dec. 31, 1975.

326. Anon., Biocides Under Wrap, Chem. Week 111, 40, Dec. 6, 1972.

327. Himel, C. M., Advance Concepts & Their Application in Insecticides Spray Efficiency (Abstract), in Ways to Increase the Efficiency and Minimize the Hazards of Pesticides Through Application Techniques & Formulation, Workshop, Fed. Working Group on Pest Management, National Agr. Library, Beltsville, MD, April 30 - May 1, 1975 (to be published).

328. Collins, R. L., Microgranules and Micro-encapsulation of Pesticides, Proc. Controlled Release Pesticide Symp., 105, Wright State University, Dayton, OH, September 8-10, 1975.

329. Scott, H. D. and Phillip, R. E., Diffusion of Selected Herbicides in Soil, Soil Sci. Soc. Amer. Proc. 36, 714, 1972.

330. Hilton, J. L., Relation of Mode of Action of Herbicides to Controlled-Release Technology, Proc. Controlled Release Pesticide Symp., 303, Wright State University, Dayton, OH, September 8-10, 1974.

331. Cardarelli, N. F., Controlled Release Elastomeric Formulations, Rep. (Abstract) Federal Working Group on Pest Management Workshop, National Agr. Library, Beltsville, MD, April 30 - May 1, 1975.

332. Allan, G. G., Neogi, A. N., Chopra, C. S. and Wilkins, R. M., Design and Synthesis of Controlled Release Pesticide Polymer Combinations, Nature (London) 234(5328), 349, 1971.

333. Allan, G. G., Chopra, C. S., Neogi, A. and Wilkins, R. M., Concept of Chemical Combination of Pesticides with Solid Waste Macromolecules, International Pest Control, 13, 10, Jan./Feb. 1971.

334. Allan, G. G., Chopra, C. S. and Wilkins, R. M., Controlled Release Pesticides Part II, The Synthesis of Herbicide - Forest Solid Waste Combinations, TAPPI, 54(8), 1293, 1971.

335. Allan, G. G., Chopra, C. S. and Russel, R. M., Controlled Release Pesticides, Part 3, Selective Suppression of Weeds and Deciduous Brush in the Presence of Conifers, International Pest Control, 14(2), 15, 1972.

336. Allan, G. G., Chopra, C. S., Maggi, M. W., Neogi, A. N. and Wilkins, R. M., Growth Enhancement of a Juvenile Conifer Forest by a Controlled Release Herbicide, International Pest Control, 15, May/June 1973.

337. Anon., New Polymers Degrade in Water, Chem. Wk. 107, 65, Sept. 2, 1970.

338. Beasley, M. L. and Collins, R. L., Water-Degradable Polymers for Controlled Release of Herbicides and Other Agents, Science, 169, 767, 1970.

339. Sinclair, R. G., Slow-Release Pesticide System, Polymers of Lactic and Glycolic Acids as Ecologically Beneficial, Cost-Effective Encapsulation Materials, Environ. Sci. Tech. 7, 955, 1973.

340. Mehltretter, C. L., Roth, C. L., Weakley, W. B., McGuire, T. A. and Russell, C. R., Potential Controlled-Release Herbicides from 2,4-D Esters oт Starches, Weed Sci. 22, 415, 1974.

341. Beasley, M. L. and Rhode, N. G., Durch Wasser Abbaubare Polymere und Verfahren zu ihr Herstellung, German Patent 2,238,912, 1973.

342. Balassa, L. L., Herbicidal Compositions and Methods of Preparing Them, U.S. Patent 3,725,031, 1973.

343. Wake, L. V., Improved Antifouling By Marine Coatings Containing Mixed Toxics, Tech. Note 363, Dept. Defense, Australian Masterials Research Lab., Maribyrnong Victoria, Australia, January 1975.

344. Feld, W. A., Post, L. K. and Harris, F. W., Controlled Release From Polymers Containing Pesticides as Pendent Substituents, Proc. Controlled Release Pesticide Symp., Wright State University, Dayton, OH, September 8-10, 1975.

345. Danielson, L. L. and Campbell, T. A., Evaluation of A Latex Based Herbicide Formulation, Rep. 41A, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

346. Geary, R. J., Particulate Pesticidal Composition Coated with An Amido-Aldehyde Resin Polymerized in Situ, U.S. Patent 3,074,845, 1973.

347. Broadhead, R. L., Alkyd Resin with Fungicidal Property, U.S. Patent 3,179,608, 1965.

348. Ugi, I., and Fetzer, U., Methods for Controlling Pests and Fungi with Polyisonitriles, U.S. Patent 3,278,371, 1966.

349. Volf, L. A., Kotetskii, V. V., Khokhlova, V. A., Konev Yu, E. and Meos, A. I., Preparation of Germicidal Polymer Materials by Ion Exchange Reaction with Antiseptics, Zhur. Prikladnoi Khimii 39(11), 2608, 1966.

350. Mills, J. T. and Schreiber, K., Use of Latex Coated Pellets for Control of Common Root Rot of Wheat, Can. J. Plant. Sci. 51, 347, 1971.

351. Hall, H., Controlled Application of Fungicide onto Onion Seed, Proc. Controlled Release Pesticide Symp., 393, Wright State University, Dayton, OH, September 8-10, 1975.

352. Cardarelli, N. F. and Major, C. J., Biocidal Rubber For Water Reclamation Systems, Rep., AMRL-TR-69-17, Air Force Systems Command, Wright-Patterson, AFB, Dayton, OH, February 1969.

353. Cardarelli, N. F., Slow Release Pesticides Utilizing Organotins, Tin. & Its Uses, No. 93, 16, 1972.

354. Greaves, J. H., Rowe, F. P., Redfern, R. and Ayres, P., Microencapsulation of Rodenticides, Nature 219, 402, July 1968.

355. Abrams, J. and Hinkes, T. M., "ESP to Control Problems of Taste and Waste, Rep. No. 7, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

356. Abrams, J. and Hinkes, T. M., Acceptability and Performance of Encapsulated Warfarin, Pest Control 14, May 1974.

357. Jackson, W. M., Use of Microencapsulation to Enhance Rodenticide Acceptance, Rep. No. 6, Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

358. Cornwall, P. B., Studies in Microencapsulation of Rodenticides, International Pest Control 12(4), 35, 1970.

359. Cardarelli, N. F. and Feldmesser, J., Controlled Release Nematicide Development: Preliminary Investigations, Proc. Controlled Release Pesticide Symp., 386, Wright State University, Dayton, OH, September 8-10, 1975.

360. Feldmesser, J., Progress Report on Controlled Release of a Nematicide, Rep. No. 32, Proc. Controlled Release Pesticide Symp., University of Akron, Akron, OH, September 16-18, 1974.

361. Fitzgerald, G. P. and Faust, S. L., Factors Affecting the Algicidal and Algistatic Properties of Copper, App. Microbiol. 11, 345, 1963.

362. Lin, C. K., Nemo, A. J. and Vedder, D. L., Copper Residue in Rainbow Trout, Hyacinth Control J., 10, 43, 1972.

363. Fitzgerald, G. P., Are Chemicals Used in Algae Control Biodegradable?, Water and Sewage Wrks., pp. 82-85, May 1975.

364. Fitzgerald, G. P. and Faust, S. L., Effect of Bacteria on the Solubility of Copper Algicides, Water & Sewage Wrks., Reprint No. 796, July 1975.

365. Cardarelli, N. F. and Bille, S. M., Evaluation of Environmental Chemicals, Inc. Controlled Release Copper Sulfate, Rep. 1, Proj. 121, Creative Biology Lab., Barberton, OH, March 1, 1976.

366. Anon., Envirocap C., Chem. Eng. News 50(23), 68, 1972.

367. Senderling, R. and Cardarelli, N. F., Protective Collars for Sheep Wear: Dept. Interior, Contract 14-16-0008-895, Denver CO, Quart. Prog. Rep., Feb. - April, 1975.

368. Cardarelli, N. F., Protective Collars for Sheep Wear, (Quart Prog.) (May - July 1975, Dept. Interior Contract 14-16-0008-895, Denver, CO, Aug. 4, 1975.

369. Cardarelli, N. F., Dermal Protective Films, U.S. Patent 3,749,772, 1973.

370. Conrady, J. A. and Stockman, C. H., Long Lasting Repellent Films for Skin and Other Substrates, U.S. Patent 3,590,118, 1971.

371. Hays, J. T., Haden, W. W. and Anderson, L. E., Nitrification of Fractions from Commercial Ureaforms, J. Agr. Food Chem. 13, 176, 1965.

372. Stansbury, R. L., Lynch, C. S. and Sor, K., Slow Release Fertilizer Composition Consisting of Asphalt Wax Binder and Inert Filler, U.S. Patent 3,276,857, 1966.

373. Lunt, O. R., Modified Sulfur Coated Granular Urea for Controlled Nutrient Release, International Congress of Soil Sci. Trans. 3, 377, 1968.

374. Rindt, D. R., Blouin, G. M. and Getsinger, J. G., Sulfur Coating on Nitrogen Fertilizer to Reduce Dissolution Rate, J. Agr. Food Chem. 16, 773, 1968.

375. Hays, T. and Hewson, W. B., Controlled Release Fertilizers by Chemical Modification of Urea: Triuret, J. Agr. Food Chem. 21, 498, 1973.

376. James, B. L., Ureaforms in Horticulture, J. Agr. Food Chem. 19, 813, 1971.

377. Smith, W. H., Underwood, H. G., and Hays, J. T., Ureaforms in the Fertilization of Young Pines, J. Agr. Food Chem. 19, 816, 1971.

378. Lunt, O. R. and Clark, S. B., Properties and Value of 1,1-diureido isobutane (IBDU) as a Long Lasting Nitrogen Fertilizer, J. Agr. Food Chem. 17, 1269, 1969.

379. Mobert, E. L., Waddington, D. V. and Duich, J. M., Evaluation of Slow Release Nitrogen Sources on Merion Kentucky Bluegrass, Soil Sci. Soc. A. Proc. 34, 335. 1970.

380. Daniel, W. H., Slow Release IBDU - Promising New Tests, Weeds, Trees, & Turf 14(1), 14, January 1975.

381. Blouin, G. M., Rindt, D. W. and Moore, O. E., Sulfur-Coated Fertilizers for Controlled Release: Pilot Plant Production, J. Agr. Food Chem. 19, 801, 1971.

382. Allen, S. E. and Mays, D. A., Sulfur-Coated Fertilizers For Controlled Release: Agronomic Evaluation, J. Agr. Food Chem. 19, 809, 1971.

383. Hasek, R. F. and Sciaroni, R. H., The Use of Osmocote Formulations in Commercial Potted Lily Production, Florists Rev. 146, 45, 1970.

384. Lunt, O. R., Controlled Release Fertilizers: Achievements and Potential, J. Agr. Food Chem. 19, 797, 1971.

385. Ohpanayikool, S., Tjia, B. and Buxton, J., Height Control of Poinsetta *Euphorbia pulcherrima* with Ethrel Drench and Slow Release Ethrel, Hortsci. 9, 300, June 1974.

386. Philen, O., Silverberg, J. and Norton, M. M., Fertilizers Containing Micro- and Macronutrients, U.S. Patent 3,520,651, 1970.

387. Herman, V. L. and Read, P. E., 3M Cap-Cyc For Controlled Growth of Petunias, Hortsci. 8(3), 281, 1973.

388. Read, P. E., Herman, V. L. and Heng, D. A., Slow Release Chlormequat: New Concept in Plant Growth Regulators, Hortsci. 9, (1) 55, February 1975.

389. Read, P. E., Bedding Plants and Vegetable Transplants, Hortsci. 7(3), 45, June 1972.

390. Attoe, O. J., Rasson, F. L., Dahnke, W. C. and Boyle, J. R., Fertilizer Release From Packets and Its Effect on Tree Growth, Soil Sci. Soc. Am. Proc. 34, 137, 1970.

391. Beale, A. F., Biuret-polyethylenimine Rosins, U.S. Patent 3,737,414, 1973.

392. Sommer, H. J., McLaren, G. A., Feichtmeir, E. F., Larsen, R. G. and Wittsell, L. E., Plant Nutrient Products, U.S. Patent 3,748,115, 1973.

393. Hyman, S., Bacteriostatic Material, U.S. Patent 3,279,986.

394. Hyman, S., Bernstein, B. S. and Kapoor, R., Activated Polymer Materials and Process for Making Same, U.S. Patent 3,876,468, 1975.

395. Hyman, S., Bernstein, B. S. and Kapoor, R., Activated Polymeric Materials and Process for Making Same, U.S. Patent 3,705,938, 1972.

396. Geary, R. J., Internal Treatment of Animals with Resin Biocidal Compositions, U.S. Patent 3,162,573, 1964.

397. Menn, J. J., Folckemer, F. B. and Miller, A., Control of Endoparasites of Animals, U.S. Patent 3,344,021, 1967.

398. Ashare, E., Brooks, T. W. and Swenson, D. W., Controlled Release From Hollow Fibers, Proc. Controlled Release Pesticide Symp. 42, Wright State University, Dayton, OH, September 8-10, 1975.

399. Passoff, P. C., Rodent Control Activities When Direct Seeding Forest Lands in Northern California, Proc. Sixth Vertebrate Pest Conf. (W. V. Johnson, ed.) Anaheim, Calif. pp. 127-131, March 5-7, 1974.

400. Walker, K., Creative Biology Lab., Barberton, OH, correspondence to McDonough, L., Yakima Agricultural Research Lab, Yakima Wash., May 20, 1975.

401. Reference deleted.

402. Anon., ALTOSID Environmental Properties, Tech. Bull., Zoecon Corp., Palo Alto, Calif., 1975.

403. Miura, T. and Takahaski, R. M., Insect Development Inhibitors. 3. Effects on Nontarget Aquatic Organisms, J. Econ. Entomol. 66, 917, 1973.

404. Anon., Altosid SR-10, Product Application Guide No. 1, Zoecon Corp., Palo Alto, Calif., 1975.

405. Giglioli, M. E. C., Low Dosage Aerial Applications of Insect Growth Regulators Against Aedes taeniorhynchus Through Dense Mangrove Canopy, (Abstract), to be Pub. Trans. Roy. Soc. Trop. Med. & Hyg. (1976).

406. Anon., Altosid IGR: Poultry Feed Through for Fly Control, Tech. Bull. Z8-04, Zoecon Corp., Palo Alto, Calif., Jan. 1975.

407. Anon., CYCOCEL^{tm} Plant Growth Regulant, Cyanamid International Co., Technical Information Bull., American Cyanamid Co., Wayne, N.J., 1965.

408. Cardarelli, N. F., "Slow Release Molluscicides and Related Materials" in Molluscicides in Schistosomiasis Control, ed. T. C. Cheng, Academic Press, N.Y., 1974.

409. Walker, E. E. and Cardarelli, N. F., Chronic Effects of Ultra Low Toxicant Concentrations, Quart, Rep. II. to National Institutes of Health, Bethesda, MD, Grant 11861-01A1 from University of Akron, Akron, OH, November 1, 1975.

410. Walker, K. E. and Cardarelli, N. F., Chronic Effects of Ultralow Toxicant Concentrations, Quart. Rep I. to National Institutes of Health, Grant No. 11861-01A1 from University of Akron, Akron, OH, August 1, 1975.

411. Kydonieus, A. F., Smith, I. K., and Hyman, S., A Polymeric Delivery System for the Controlled Release of Pesticides: Hercon^{tm} Roach Tape, Rep. Health Chem. Corp., New York, N.Y., 1974.

412. Anon., Controlled-Release Pesticides Attract Interest, Chem. & Eng. News, 52, 20, 1974.

413. Beroza, M., Beroza Associates, Inc. Silver Spring, MD, Interview with Kydonieus, A., Herculite Protective Fabric Corp., Notes, September 26, 1975.

414. Schmolesky, G. E., WARF Rept. No. 3113988, Wisconsin Alumni Research Foundation, Madison, Wisconsin, January 14, 1974.

415. Schmolesky, G. E., WARF Rept. No. 4070491 IV, Wisconsin Alumni Research Foundation, Madison, Wisconsin, September 8, 1975.

416. Folckemer, F. B., Hanson, R. E. and Miller, A., Resin Compositions Comprising Organophosphorus Pesticides, U.S. Patent 3,318,769, 1967.

417. Gillett, J. W., et al., Evaluation of Human Health Hazards on Use of Dichlorvos (DDVP), Especially in Resin Strips, Residue Rev. 44, 115, 1972.

418. Anon., Pesticide Strip Toxic? No Hook to Hang It On, Med. World News 11(1), 4, Jan. 2, 1970.

419. Anon., Crosslinked Nylon-Type Encapsulating Polymer. Exemption from the Requirement of a Tolerance, Fed. Reg. 240315, Vol. 39(52) 9965-6.

420. Ritch, J. B., Crosslinked Nylon-Type Encapsulating Polymer; Proposed Exemption from Requirement of a Tolerance, Fed. Reg. 40(149), Fri., August 1, 1975.

421. Ivy, E. E., Pencap M: An Improved Methyl Parathion Formulation, J. Econ. Entomol. 65, 473, 1972.

422. Beroza, M., Beroza and Associates Inc., Silver Spring, MD, Interview Notes, Interview with Pennwalt Corp. Personnel, King of Prussia, PA, Sept. 29, 1975.

423. Bernstein, B. S., Hyman, S., and Kapoor, R. C., Activated Polymeric Materials and Processes for Making the Same, U.S. Patent 3,857,934, 1974.

424. Wolfe, W., Europeans Examine U.S. Implant System, Weeds, Trees, and Turf, 14, August 1975.

425. Smith, E., Preventing Pin Oak Chlorosis, Woodlands Mag. 13(1), November 1974-January 1975.

426. Wolfe, W., 'Creative' Cure for Chlorosis, Weeds, Trees and Turf, July 1975.

427. Carpenter, P. L. and McNiel, R. E., A New Method of Fertlizing Trees and Shrubs, Rep. Purdue University Agriculture Experiment Station, Dept. Horticulture, Lafayette, Ind.

428. Hurlbert, S. H., Mulla, M. S. and Willson, H. R., Effects of an Organophosphorus Insecticide on the Phytoplankton and Insect Populations of Fresh Water Ponds, Ecological Monographs 42(3), 269, 1972.

429. Seymour, K. G., Pesticide Formulation With Polymers, Federal Working Group on Pest Management Workshop, National Agr. Library, Beltsville, MD, April 30-May 1, 1975.

430. Anon., Advanced Lubrication Material May Permit Long-Life Parts, Product Engineering, 27, August 1974.

431. Christy, R. I. and Meeks, C. R., Polyurethane Retainers for Ball Bearings, International Ball Bearing Symp., Charles Stark Draper Laboratory, Cambridge, Mass., June 5-7, 1973.

432. Taschenberg, E. F. and Roelofs, W. L., Pheromone Communication Disruption of the Grape Berry Moth with Microencapsulated and Hollow Fiber Systems, Rept. N.Y. Agri. Exp. Stn., Geneva, N.Y. Submit. to J. Environ. Entomol. for Publ., 1976.

433. Brooks, T. W., Ashare, E. and Swenson, D. W., Hollow Fibers as Controlled Vapor Release Devices, Paper Pres. to Amer. Chem. Soc. Mtng., New York, New York, April 9, 1976 (to be published).

434. Krieg, J. P., Combatting Crawling Insects with Hercon^{tm} Controlled Release Pesticide Applications, Rep. Health-Chem Corp., New York, N.Y., 1974.

435. Beroza, M., Gentry, C. R., Blythe, J. L., and Unischik, G. M., Isomer Content and Other Factors Influencing Captures of Oriental Fruit Moth by Synthetic Pheromone Traps, J. Econ. Entomol. 66, 1307-1311 (1973).

436. Anon., Controlled Release Insecticides, Soap/Cosmetics/Chem. Specialties, 1, March 1975.

437. Nichols, L. D., Process of Preparing Gelled Cellulose Triacetate Products and the Products Produced Thereby, U.S. Patent 3,846,404, 1974.

438. Anon., Sustrelle^{tm} Information Sheet, Moleculon Res. Corp., Cambridge, MA, 1975.

439. Nichols, L. D., Poroplastic and Sustrelle: Controlled Release Vehicles Having Broad Compatibility with Dissolved and Precipitated Pesticides, Proc. Controlled Release Pesticide Symp., 95, Wright State University, Dayton, OH, September 8-10, 1975.

440. Anon., Sustrelle Laboratory Manual, Moleculon Research Corp., Cambridge, Mass., June 2, 1975.

441. Vandegaer, J. E., ed., Microencapsulation: Processes and Applications, Plenum Pub. Corp., 1974.

442. Leeflang, K. W. H., Biologic Degradation of Rubber Gaskets Used for Sealing Pipe Joints, J. Am. Waterworks Assoc., 60, 1070, 1968.

443. Heap, W. M. and Morrell, S. H., Microbiological Deterioration of Rubbers and Plastics, J. Appl. Chem. 18(7), 189, 1968.

444. Maclachlan, J., Heap, W. M. and Pacitti, J., Attack of Bacteria and Fungi on Rubbers and Plastics in the Tropics, Monogr. Soc. Chem. Industry 23, 185, 1966.

445. Rook, J. J., Microbiological Deterioration of Vulcanized Rubber, Appl. Microbiol. 3(5), 302, 1955.

446. Rytych, R. J., Fungicides and Bactericides for Use in Rubber, International Biodeterioration Bull. 5(1), 3, 1969.

447. Ross, R. T., Biodeterioration of Paint and Paint Films, J. Paint Technol., 41, 266, 1969.

448. Kazuki, K., Fungus Resistance, Nippon Gomu Kyokaishi 38 (10), 969, 1965.

449. Kost, A. N., et. al., Action of Phenols on Rubber Destroying Microorganisms, Vestnik Moskov, Univ. Ser. Mat. Mekh. Astron. Fizi Khim. 14(3), 213, 1959; Chem. Abs. 54, 13708d, 1960.

450. Geldof, H., Resistance of Natural and Synthetic Rubber Against Microbiological Attack, Proc., Techn. Seminar Industrial Rubber Manufacturers Research Assoc., pp. 89-97, 1966, Chem. Abs. 70, 12382, 1969.

451. Cunddell, A. M. and Mulcock, A. P., The Effect of Curing Agent Concentration on the Microbiological Deterioration of Vulcanized Natural Rubber, International Biodeterioration Bull. 9(4), 91, 1973.

452. Thaysen, A. C., Bunker, H. J. and Adams, M. E., Nature (London) 155, 322, 1945.

453. Dunn, P. and Hart, S. J., The Tropical Deterioration of Rubber, J. International Rubber Institute, 3(2), 81, 1969.

454. Zwicker, B. M. G., B. F. Goodrich Chem. Co., Cleveland, OH, Correspondence to Cardarelli, N. F., University of Akron, Akron, OH, Dec. 15, 1975.

455. Anon., NORDEL Hydrocarbon Rubber, E. I. duPont Co. Brochure A-76922, Jan. 1973.

456. Monk, D. W., Biodegradability of Cellophane, Modern Packaging, p. 43, April, 1974.

457. Anon., Code of Fed. Reg. No. 21, parts 10-129, Subpart B, Sect. 121.101 (h), April 4, 1973.

458. Gay, F. J. and Wetherly, A. H., Laboratory Studies of Termite Resistance, IV. The Termite Resistance of Plastics, Australian Commonwealth Sci. & Ind. Research Org., Div. Entomol., Tech. Paper #5, 1962.

459. Rosato, D. V., Other Properties and Characteristics, Chap. 8 in Environmental Effects on Polymeric Materials, ed. Rosato, D. V. and Schwarz, R. T., Vol. I, Intersci. Publ., New York, N.Y., 1968.

460. Anon., Kraton: Thermoplastic Rubber Crumb. Brochure, Shell Chemical Co., Houston, Texas, 1972.

461. Blake, J. T., Kitchin, D. W. and Pratt, O. S., Appl. Microbiol. 3, 35, 1955.

462. Secard, D. L., Correspondence to Steller, R. L., both of B. F. Goodrich Chem. Co., "Cardarelli Request for Environmental Impact of Carboset Resins," November 6, 1975.

463. Wright, W. W., Fluorocarbon Polymers in Monographs in Macromolecular Chemistry, pp. 287-346, ed. R. T. Conley, Vol. I., Marcel Dekker Pub., N.Y., 1970.

464. Conley, R. T. and Guadiana, R. A., Polyamides, Polyesters and Polyethers, pp. 413-451, Ibid.

465. Heap, W. M. and Morrell, S. H., Microbiological Deterioration of Rubbers and Plastics, J. Appl. Chem., 18(7), 189, 1968.

466. Kulman, F. E., Microbiological Deterioration of Buried Pipe and Coatings, Corrosion, 14, 23, 1958.

467. Anon., Hypalon: Engineering Properties, Brochure E. I. duPont Co., 1975.

468. Booth, G. H. and Robb, J. A., Bacterial Degradation of Plasticised PVC - Effect on Some Physical Properties, J. Appl. Chem. 18, 194, July 1968.

469. MacLachlin, J., Heap, W. M. and Pacitti, J., Attack of Bacteria and Fungi on Rubbers and Plastics in the Tropics, Monograph, Soc. Chemistry Industry 23, 185, 1966.

470. Anon., Neoprene: Engineering Properties, Brochure E. I. duPont Co., Wilmington, Delaware, 1975.

471. Anon., Celcon: Acetal Copolymer, Bull. Celanese Plastics Co., Chatham, New Jersey, May 1975.

472. Fine, S. D., Microporous Polymeric Filters, Fed. Reg. 40, No. 119, Title 21, Cl, Part 121, F., Thurs., June 19, 1975.

473. Conway, F., Microporous Plastics Promise a New Era in Filtration, Plast. Eng. 31 (2), February 1975.

474. Beroza, M., Bierl, B. A., James, P. and DeVilbiss, D., Measuring Emission Rates of Pheromones from Their Formulations, J. Econ. Entomol. 68, 369, 1975.

475. Husted, R. F. and Radke, R. O., Herbicidal Compositions, U.S. Patent 3,834,891, 1974.

476. Coppedge, J. R., Lindquist, D. A., Bull., D. L. and Dorough, H. W., Fate of 2-methyl-2-(methylthio) Propionaldehyde O-(methyl-carbamoyl) Oxime in Cotton Plants and Soil, J. Agr. Food Chem. 15, 902, 1967.

477. Fitzgerald, G. P., Compatibility of Swimming Pool Algicides and Bactericides, Water & Sewage Works, 115, February 1968.

478. Anon., Pesticide Program: Gudelines for Registering Pesticides in United States, Fed. Reg. 40, No. 123, Part II 26802-26928, Wed., June 25, 1975.

479. Sanborn, J. R., The Fate of Select Pesticides in the Aquatic Environment, EPA-660/3-74-025, Dec. 1974.

480. Freed, V. H. and Haque, R., Adsorption, Movement and Distribution of Pesticides in Soils, Chapt. 10, 441-460 in Pesticide Formulations, ed. Wade VanValkenburg, Marcel Dekker, Inc., New York, N.Y., 1973.

481. Levitt, J., Responses of Plants to Environmental Stresses, Academic Press, New York, N.Y., 1972.

482. Treshow, M., Environmental and Plant Responses, McGraw-Hill Book Co., New York, New York, 1970.

483. Middeln, C. H. Van., Assay Procedures for Pesticide Residues, in Pesticides in the Environment, Vol. I., Part II, pp. 309-400, ed. R. White-Stevens, Marcel-Dekker Pub. Co., New York, N.Y., 1971.

484. Bukovac, M. J., Foliar Penetration of Pesticide Chemicals, Rep. Pesticide Research Center, Michigan State University, East Lansing, Mich., pp. 73-75, 1974.

485. Loeffler, J. E. and Overbeek, J. Van., Metabolism of Herbicides in Pesticides in the Environment, Vol. I, Part 1, p. 237-250, ed. R. White-Stevens, Marcel-Dekker Pub. Co., New York, N.Y., 1971.

486. Anon., Principles of Plant and Animal Control, Vol. II, Nat. Acad. Sci., Washington, D.C., 1975.

487. Ahuja, et. al., Chemical Analysis of the Environment, Plenum Press, New York, N.Y., 1973.

488. Hess, E. H. and Albright, F. R., Unique Analytical Problems Associated with the Controlled Release Approach, Proc. Controlled Release Pesticide Symp., Rep. No. 16, University of Akron, Akron, OH, September 16-18, 1974.

489. Baker, R. W. and Lonsdale, H. K., Controlled Delivery - An Emerging Use for Membranes, Chemtech., 5, 668, Nov. 1975.

490. Cardarelli, N. F. and Kanakkanatt, S. V., Reduction of Water Contamination Through the Use of Controlled Release Pesticides, Proc. Second World Congress on Water Resources, New Delhi, India, Vol. 6B, 12-16 December 1975.

491. Tanquary, A. C. and Lacey, R. E., ed., Controlled Release of Biologically Active Agents, Plenum Press, New York, N.Y., 1974.